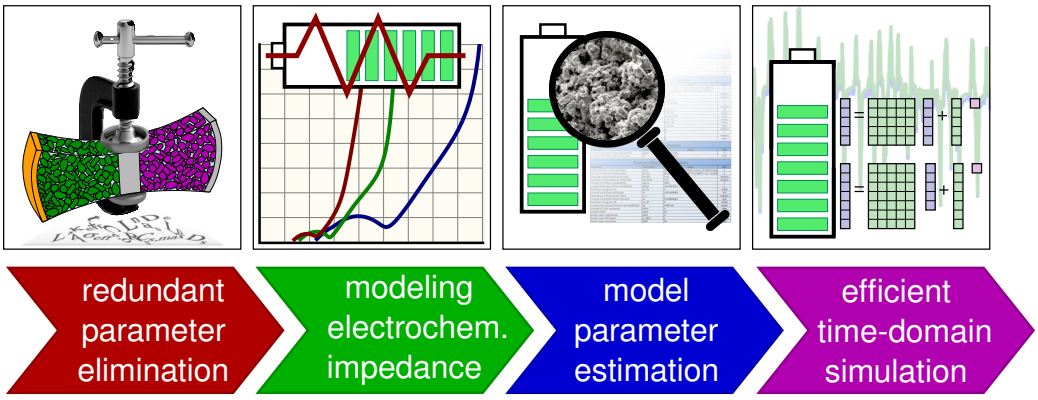
MODELING ELECTROCHEMICAL IMPEDANCE

2.1: More detail required at the solid/electrolyte interface

- We have eliminated redundant model parameters so we are now (theoretically) able to estimate values for the remaining parameters from laboratory-based cell input/output measurements (Ch. 3).

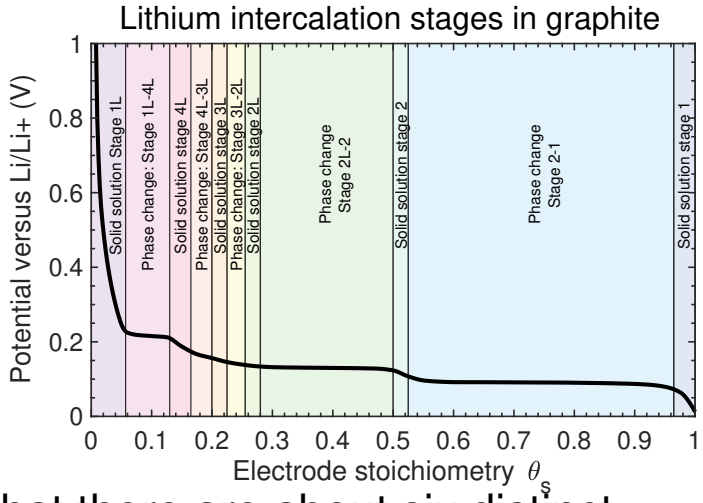


- Our next step is to develop impedance models. They:
  - Will be used as part of the parameter-estimation process,
  - Give a lot of insight by themselves,
  - Are also used when converting PDEs to time-domain ROMs.
- Cell-level impedance models are based on transfer functions (TFs) of individual electrochemical variables with respect to input current.
  - Very similar to what you learned in Ch. 6 of ECE5710.
  - But, some improvements have been made to derivation since then.
  - Also, we must add a description of some dynamic effects not yet considered by prior physical models.

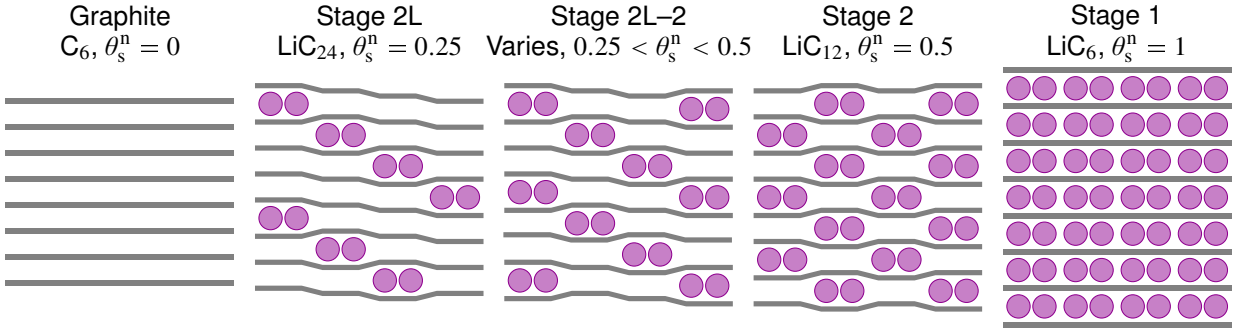
- We will enhance the standard Doyle–Fuller–Newman (DFN) model in five significant ways:
  1. We replace the standard Butler–Volmer kinetics with the multi-species-multi-reaction (MSMR) model.
  2. We add a description of an electrical double-layer to the electrode/electrolyte interface.
  3. We incorporate constant-phase elements (CPEs) in the interface double-layer description.
  4. We incorporate CPEs in the solid-diffusion description.
  5. We add SOC-dependence to electrode solid diffusivity.
- In this chapter:
  - We first develop these enhancements to the standard DFN model.
  - Then, we present a full-cell impedance model.
  - Appendices derive TFs for all cell electrochemical variables and share some details that are helpful when implementing the TFs.
- Comment: In the equations, I will generally suppress the generic region superscript "r" to simplify the notation.

2.2: Upgrade 1: Multi-species-multi-reaction (MSMR) model

- The DFN Butler–Volmer kinetics equation depends on electrode OCP.
  - This OCP can be a completely general function of stoichiometry.
  - Implicitly, this assumes a single reaction at the particle surface.
  - Data from physical cells do not always agree with this assumption.
- Here, we introduce the MSMR model, which computes the overall OCP function as a composite of multiple simpler OCP functions.
- Each simpler OCP function represents an independent reaction, filling and emptying different "galleries" in electrode's host material.
- The model is motivated by noticing the flat regions of some OCP curves (esp. graphite).
  - These regions correspond to a phase-change region.
  - Sloped regions correspond to single-phase reactions.



- From the figure, we might guess that there are about six distinct "reactions" with intermediate phase-change regions in graphite.
- The figure below visualizes what is happening: Li is "staging" between graphene sheets in graphite for different levels of θ_s:

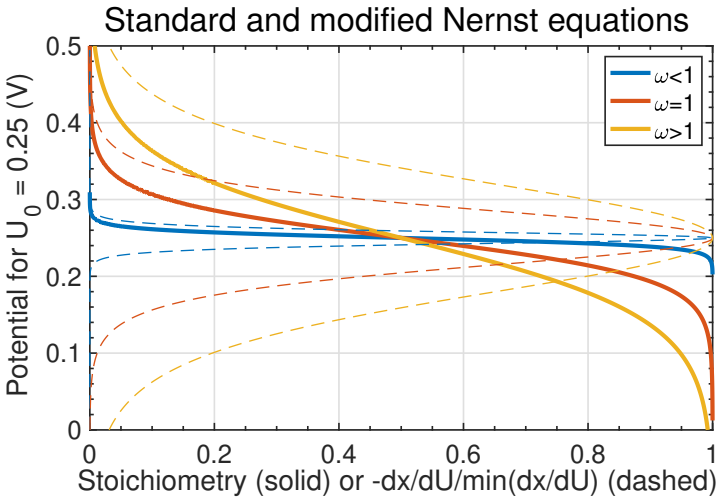


(Lattice distortion due to intercalation is real, but amount is exaggerated in this figure)

- There are different “stages” in the figure corresponding to “empty”, “one quarter full”, “one third full”, “half full”, and “full”.
- Notice that patterns form; lithium does not tend to distribute randomly.
  - Near any of these more stable patterns is a “single-phase” region.
  - Moving between these patterns is a “phase change” region.
- The electrochemical reaction for gallery j can be expressed as:

$$\mathrm{Li}^+ + \mathrm{e}^- + \mathrm{Host}_j \rightleftharpoons (\mathrm{Li\text{-}Host})_j \,,$$

  where “Host” is a vacant site and $(\mathrm{Li\text{-}Host})$ is filled: for each gallery j, an individual unfilled host site can hold one Li to become a filled site.
- For gallery j, $0 < X_j \leq 1$ is the fraction of (both filled and unfilled) available sites and $0 \leq x_j \leq X_j$ is the fraction of filled sites $(\mathrm{Li\text{-}Host})_j$.
  - The normalized total of available sites is one: $\sum_j X_j = 1$.
- The equilibrium potential is then represented by a modified Nernst equation (below), where $f = F/(RT)$, ω_j is a unitless shape factor, and U_j^0 is a concentration-independent potential:

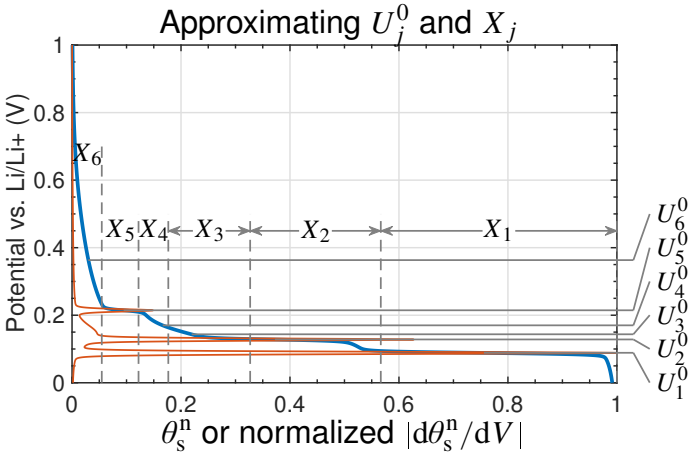


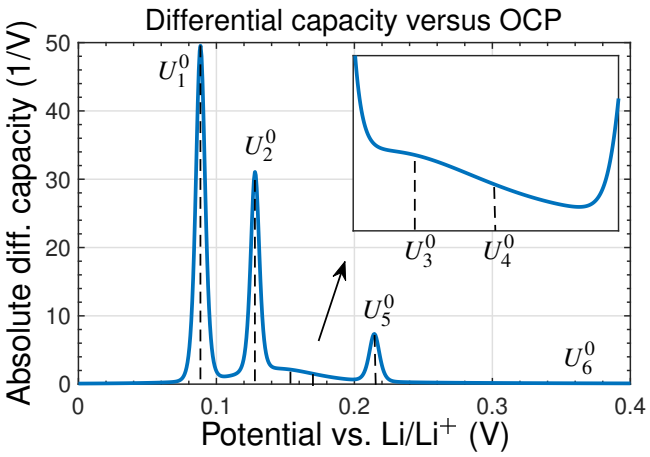
$$U_j = U_j^0 + \frac{\omega_j}{f} \ln\left(\frac{X_j - x_j}{x_j}\right) = U_j^0 + \frac{\omega_j}{f} \ln\left(\frac{x_{\mathrm{unfilled},j}}{x_{\mathrm{filled},j}}\right),$$

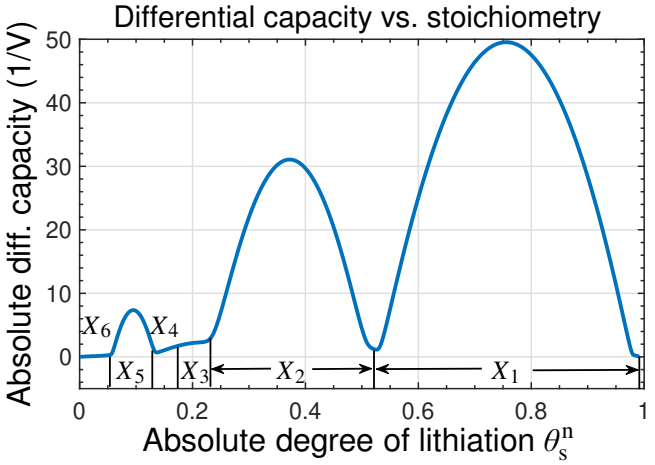
- The following are physical properties for these quantities:
  - *In equilibrium*, the $\{x_j\}$ are fixed, the potentials of each gallery are equal (i.e., $U_j = U_{\mathrm{ocp}}$) and U_{ocp} is affine in temperature T.

- The logarithmic term infers that potential will approach $+\infty$ when the gallery is empty and $-\infty$ when the gallery is completely filled.[1]
- ω_j models the nature of the reaction on a continuum:
  - $\omega_j = 0$ represents ideal two-phase behavior (stair-like potential);
  - $\omega_j = 1$ represents ideal single-phase behavior (classic Nernst);
  - $\omega_j > 1$ represents disordered behaviors.

- We can "read" approximate values for X_j, U_j^0, and ω_j from the OCP and differential-capacity (dQ/dV) curves.
- Helps to initialize optimizations to find MSMR parameter values to match data from electrode having unknown composition.
- U_j^0 are OCP plateau voltages; X_j are plateau widths.







- The number of reactions is equivalent to the number of peaks in the dQ/dV plot (it is sometimes difficult to see them all).

[1] There are practical limits due to other chemical reactions not considered here: copper oxidizes at around 3.4 V with respect to Li/Li$^+$ in common electrolytes; lithium plates at around 0 V; many electrolytes break down at voltages above about 4.3 V.

- Potentials U_j^0 are the peak locations in a $\partial\theta_\mathrm{s}/\partial U_\mathrm{ocp}$ against U_ocp plot.
- Gallery size X_j are peak widths in a $\partial\theta_\mathrm{s}/\partial U_\mathrm{ocp}$ against θ_s plot.
- Can find ω_j by looking at peak heights in (unnormalized) dQ/dV plot:

$$\left.\frac{\partial x_j}{\partial U}\right|_{U=U_j^0, x_j=X_j/2} = -\frac{f}{4}\frac{X_j}{\omega_j}.$$

- We can invert the potential equation to find the "filled" site fractions at the solid/electrolyte interface ("s, e") at any local potential U:

$$x_{\mathrm{s,e},j} = \frac{X_j}{1+\exp\left[f(U-U_j^0)/\omega_j\right]}.$$

- The electrode surface stoichiometry, $\theta_\mathrm{s,e}$, is then found by summing the fractional occupancies from all galleries:

$$\theta_\mathrm{s,e} = \sum\nolimits_j x_{\mathrm{s,e},j} = \sum\nolimits_j \frac{X_j}{1+\exp\left[f(U-U_j^0)/\omega_j\right]}.$$

- Corresponding differential-capacity can be computed analytically:

$$\frac{\partial\theta_\mathrm{s,e}}{\partial U} = -\sum\nolimits_j \frac{f X_j \exp\left[f(U-U_j^0)/\omega_j\right]}{\omega_j\left\{1+\exp\left[f(U-U_j^0)/\omega_j\right]\right\}^2}.$$

- In equilibrium, $U = U_\mathrm{ocp}$, $x_{\mathrm{s,e},j} = x_{0,j}$, and $\theta_\mathrm{s,e} = \theta_{\mathrm{s},0}$.
- When cell is not in equilibrium, galleries fill and empty independently, modeled via separate Butler–Volmer equations, where $i_\mathrm{f} = \sum_{j=1}^{J} i_{\mathrm{f},j}$:

$$i_{0,j} = \bar{k}_{0,j}(x_j)^{\omega_j\alpha_j}(X_j - x_j)^{\omega_j(1-\alpha_j)}\theta_\mathrm{e}^{(1-\alpha_j)}$$

$$i_{\mathrm{f},j} = i_{0,j}\left[\exp((1-\alpha_j)f\eta) - \exp(-\alpha_j f\eta)\right].$$

  - This adds a nonlinearity to the model.

- Each gallery has own solid-diffusion equation (where $\theta_\mathrm{s} = \sum_{j=1}^{J} x_j$):

$$\frac{\partial x_j}{\partial t} = \frac{1}{\tilde{r}^2}\frac{\partial}{\partial\tilde{r}}\left(\bar{D}_\mathrm{s}\tilde{r}^2\frac{\partial x_j}{\partial\tilde{r}}\right) \qquad \text{and} \qquad \left.\bar{D}_\mathrm{s}\frac{\partial x_j}{\partial\tilde{r}}\right|_{\tilde{r}=1} = -\frac{|\theta_{100}-\theta_0|}{10\,800\,Q} i_{\mathrm{f},j}.$$

2.3: Upgrade 2: Electrical double layer

- The DFN model defines electrode particle surface overpotential η as:

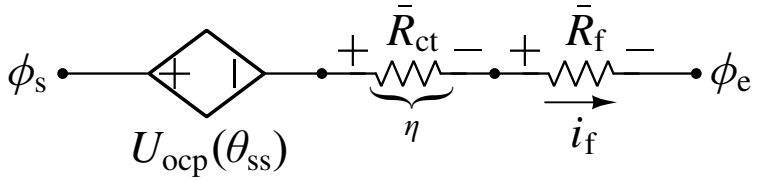
$$\eta = \phi_\mathrm{s} - \phi_\mathrm{e} - U_\mathrm{ocp}(\theta_\mathrm{ss}) - \bar{R}_\mathrm{f} i_\mathrm{f}.$$

  - $\theta_\mathrm{ss}(\tilde{x}, t) = \theta_\mathrm{s}(\tilde{x}, 1, t)$, i.e., surface stoichiometry, but can't call it $\theta_\mathrm{s,e}$ any longer since we will be modeling more detail at the interface.

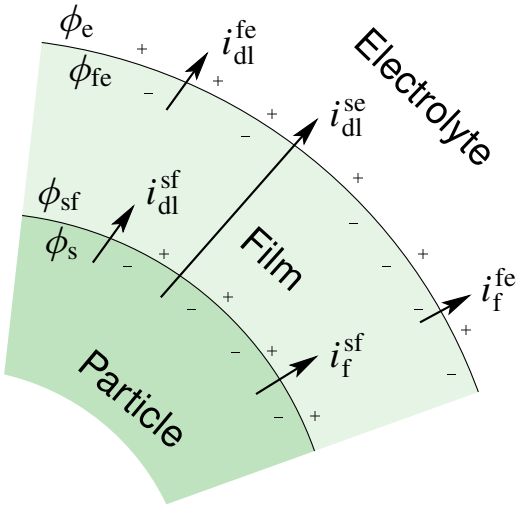
- We can re-arrange this expression to get:

$$\phi_\mathrm{s} = U_\mathrm{ocp}(\theta_\mathrm{ss}) + \eta + \bar{R}_\mathrm{f} i_\mathrm{f} + \phi_\mathrm{e}.$$

- This interfacial model can be *visualized* as an equivalent circuit:



- DFN model was originally derived to describe constant-current (not transient) response of a lithium-ion cell.
- When identifying a model for physical cells, we find that this interfacial model is overly simplistic: We must add double-layer capacitance to describe transient behaviors better.
- We will now consider a more general model of the solid–electrolyte interface.
- Include possibility of a particle surface film, having resistance $\bar{R}_\mathrm{f}$, as before.
- But, add "double layer" of charges at different interfaces, describing ordering of charged ions in the electrolyte.



- These double layers of charge can be modeled as capacitances.

- Many double-layer models have been proposed in the literature—there is no consensus regarding which is correct or "best".
- Will introduce one of the most general models[2], and you will learn that it is straightforward to substitute a different model if desired.
- In the illustration, the particle surface has electric potential ϕ_{s}; film at particle/film interface has potential ϕ_{sf}; film at film/electrolyte interface has potential ϕ_{fe}; electrolyte at film interface has potential ϕ_{e}.
- Both interfaces are considered to have a faradaic (non-capacitive) lithium flux modeled by a Butler–Volmer/MSMR relationship:

$$i_{\mathrm{f}} = \sum_{j=1}^{J} i_{0,\mathrm{j}} \left\{ \exp\left((1-\alpha) f \left(\phi_1 - \phi_2 - U_j\right)\right) - \exp\left(-\alpha f \left(\phi_1 - \phi_2 - U_j\right)\right) \right\}.$$

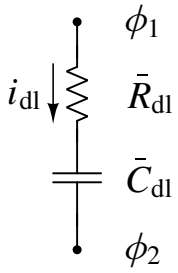
  - ϕ_1 is potential of the phase closest to (or same as) the particle.
  - ϕ_2 is potential of the phase closest to (or same as) the electrolyte.
  - U_j is the open-circuit potential of the charge-transfer reaction.
- Interfaces between ϕ_{s} and ϕ_{sf}, between ϕ_{fe} and ϕ_{e}, as well as overall film (between ϕ_{s} and ϕ_{e}) are also assumed to develop a nonfaradaic (capacitive) lithium flux that arises from the charging and discharging of an electrochemical double-layer at that interface.
- If capacitance at this interface is considered to be ideal, we can model lithium flux for any of these interfaces generically as:

$$i_{\mathrm{dl}} = \bar{C}_{\mathrm{dl}} \frac{\partial(\phi_1 - \phi_2)}{\partial t},$$

  where double-layer capacitance $\bar{C}_{\mathrm{dl}}$ is measured in farads.

[2] From: Meyers, J.P., Doyle, M., Darling, R.M., and Newman, J., "The impedance response of a porous electrode composed of intercalation particles", *Journal of the Electrochemical Society*, 147(8), 2000, 2930–40.

- However, we will later want to consider a more realistic double layer that also has a series resistance $\bar{R}_{\rm dl}$ (measured in ohms).
- Consider the circuit to the right; analyze in the Laplace domain:



$$\Phi_1(s) - \Phi_2(s) = I_{\rm dl}(s) Z_{\rm dl}(s) = I_{\rm dl}(s) \left[\bar{R}_{\rm dl} + \frac{1}{s\bar{C}_{\rm dl}} \right].$$

- Rearrange:

$$s\bar{C}_{\rm dl}(s)(\Phi_1(s) - \Phi_2(s)) = I_{\rm dl}(s) \left[s\bar{R}_{\rm dl}\bar{C}_{\rm dl} + 1 \right].$$

- Convert to time domain:

$$\bar{C}_{\rm dl} \frac{\partial(\phi_1(t) - \phi_2(t))}{\partial t} = \bar{R}_{\rm dl}\bar{C}_{\rm dl} \frac{\partial i_{\rm dl}(t)}{\partial t} + i_{\rm dl}(t).$$

- This reduces to the ideal case when $\bar{R}_{\rm dl}$ is zero.
- Otherwise, the resistance and capacitance combine to form a time constant that models non-instantaneous charge-carrier movement in the double layer.
- Summary of notation regarding interfacial fluxes:
  - Faradaic flux from electrode to electrolyte is $i_{\rm f}$.
  - Nonfaradaic double-layer flux is $i_{\rm dl}$.
  - Total flux is $i_{\rm f+dl}$.

2.4: Ideal interfacial impedance model

- With these two model upgrades, we seek to derive the small-signal impedance of the solid/electrolyte interface, including double layer(s).

Impedance at the particle/film interface

- We first investigate the impedance at the particle/film interface.
- Recall, diffusion of lithium in a particle is modeled via Fick's law as:

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

  where the nonzero boundary condition *has been* written as:

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

- We must now consider whether lithium flux through particle surface is faradaic only, or whether it also has a nonfaradaic component.
  - Following Meyers, we assume that it remains *only faradaic* since no lithium crosses interface due to double-layer charging.
  - Excess surface double-layer charge is due to electron flow only.
- Because we now consider multiple interfaces, we rewrite $i_{\mathrm{f},j}$ as $i_{\mathrm{f}.j}^{\mathrm{sf}}$.
  - Temporary superscript "sf" denotes "from 's' to 'f' phases".
- Recall Jacobsen–West TF from ECE5710 (where $\tilde{x}_\mathrm{ss} = x_\mathrm{ss} - x_{\mathrm{s},0}$):

$$\widetilde{X}_{\mathrm{ss},j}(s) = \frac{|\theta_{100}-\theta_0|}{10\,800\bar{D}_\mathrm{s}Q}\left[\frac{1}{1-\sqrt{s/\bar{D}_\mathrm{s}}\coth\left(\sqrt{s/\bar{D}_\mathrm{s}}\right)}\right]I_{\mathrm{f},j}^{\mathrm{sf}}(s).$$

- We sum both sides of this equation over all j and find:

$$\widetilde{\Theta}_\mathrm{ss}(s) = \frac{|\theta_{100}-\theta_0|}{10\,800\bar{D}_\mathrm{s}Q}\left[\frac{1}{1-\sqrt{s/\bar{D}_\mathrm{s}}\coth\left(\sqrt{s/\bar{D}_\mathrm{s}}\right)}\right]I_\mathrm{f}^{\mathrm{sf}}(s).$$

- We solve for $I_{\rm f}^{\rm sf}(s)$ by linearizing the equations describing the kinetics at the electrode/electrolyte interface.
- Here, we replace the standard Butler–Volmer kinetics with the kinetics description from the MSMR model.
  - The overpotential at the particle surface can be written as:

$$\eta = \phi_{\rm s} - \phi_{\rm sf} - U_{\rm ocp}(\theta_{\rm s}).$$

  - The exchange current density for gallery j can be expressed as:

$$i_{0,j} = \bar{k}_{0,j}(x_j)^{\omega_j\alpha_j}(X_j - x_j)^{\omega_j(1-\alpha_j)}\theta_{\rm e}^{(1-\alpha_j)}.$$

  - Finally, the overall faradaic flux out of the particle is expressed as:

$$i_{\rm f}^{\rm sf} = \sum_{j=1}^{J} i_{0,j}\left[\exp((1-\alpha_j)f\eta) - \exp(-\alpha_j f\eta)\right].$$

- We linearize $i_{\rm f}^{\rm sf}$ by forming a Taylor-series expansion around setpoint:

$$p^* = \{x_j = x_{j,0}, \theta_{\rm e} = \theta_{\rm e,0} = 1, \phi_{\rm s} - \phi_{\rm sf} = U_{\rm ocp}(\theta_{\rm s,0}), i_{\rm f}^{\rm sf} = 0\}$$

  and discarding second- and higher-order terms (also, $\theta_{\rm s,0} = \sum_{j=1}^{J} x_{j,0}$).
- To do so, we require the derivatives:

$$\left.\frac{\partial i_{\rm f}^{\rm sf}}{\partial \phi_{\rm sf}}\right|_{p^*} = f\underbrace{\left[\sum_{j=1}^{J}\bar{i}_{0,j}\right]}_{\bar{i}_0} \qquad \text{and} \qquad \left.\frac{\partial i_{\rm f}^{\rm sf}}{\partial x_j}\right|_{p^*} = -f[U_{\rm ocp}]'\bar{i}_0,$$

  where we have replaced the DFN definition of $\bar{i}_0$ with a new definition $\bar{i}_0 = \sum_{j=1}^{J}\bar{i}_{0,j}$ for the MSMR model, and where:

$$\bar{i}_{0,j} = \bar{k}_{0,j}(x_{0,j})^{\omega_j\alpha_j}(X_j - x_{0,j})^{\omega_j(1-\alpha_j)}$$

$$[U_{\rm ocp}]' = \left.\frac{\partial U_{\rm ocp}(\theta_{\rm s})}{\partial\theta_{\rm s}}\right|_{\theta_{\rm s,0}}.$$

- With these terms, we can write (where $\tilde{\phi}_\mathrm{s} = \phi_\mathrm{s} - U_\mathrm{ocp}(\theta_{\mathrm{s},0})$):

$$\begin{aligned} i_\mathrm{f}^\mathrm{sf} &\approx f\bar{i}_0\left(\phi_\mathrm{s} - \phi_\mathrm{sf} - U_\mathrm{ocp}(\theta_{\mathrm{s},0})\right) - f\bar{i}_0[U_\mathrm{ocp}]'\sum_{j=1}^{J}\left(x_{\mathrm{ss},j} - x_{j,0}\right) \\ &= f\bar{i}_0\left(\tilde{\phi}_\mathrm{s} - \phi_\mathrm{sf}\right) - f\bar{i}_0[U_\mathrm{ocp}]'\sum_{j=1}^{J}x_{\mathrm{ss},j} + f\bar{i}_0[U_\mathrm{ocp}]'\sum_{j=1}^{J}x_{j,0} \\ &= f\bar{i}_0\left(\tilde{\phi}_\mathrm{s} - \phi_\mathrm{sf}\right) - f\bar{i}_0[U_\mathrm{ocp}]'\left(\theta_\mathrm{ss} - \theta_{\mathrm{s},0}\right). \end{aligned}$$

- This can be rearranged in terms of debiased $\tilde{\phi}_\mathrm{s}$ and ϕ_sf as:

$$\tilde{\phi}_\mathrm{s} - \phi_\mathrm{sf} = \bar{R}_\mathrm{ct}^\mathrm{sf} i_\mathrm{f}^\mathrm{sf} + [U_\mathrm{ocp}]'\tilde{\theta}_\mathrm{ss},$$

  where $\bar{R}_\mathrm{ct}^\mathrm{sf} = 1/(f\bar{i}_0)$.[3]

- Taking Laplace transforms, we have:

$$\widetilde{\Phi}_\mathrm{s} - \Phi_\mathrm{sf} = \bar{R}_\mathrm{ct}^\mathrm{sf} I_\mathrm{f}^\mathrm{sf} + [U_\mathrm{ocp}]'\widetilde{\Theta}_\mathrm{ss}.$$

- At this point, we can define ideal particle diffusion impedance $\bar{Z}_\mathrm{s}(s)$:

$$\bar{Z}_\mathrm{s}(s) = [U_\mathrm{ocp}]'\frac{|\theta_{100} - \theta_0|}{10\,800\bar{D}_\mathrm{s}Q}\left[\frac{1}{1 - \sqrt{s/\bar{D}_\mathrm{s}}\coth\left(\sqrt{s/\bar{D}_\mathrm{s}}\right)}\right].$$

- Substituting this in the Jacobsen–West transfer function, we have:

$$\widetilde{\Phi}_\mathrm{s} - \Phi_\mathrm{sf} = (\bar{R}_\mathrm{ct}^\mathrm{sf} + \bar{Z}_\mathrm{s})I_\mathrm{f}^\mathrm{sf}.$$

- The interface also supports a lithium flux due to the double layer:[4]

[3] Note that if we use a standard DFN kinetics model instead of an MSMR model, this definition of $\bar{R}_\mathrm{ct}^\mathrm{sf}$ still applies, and $\bar{i}_0$ is the exchange current density of the standard DFN kinetics instead of the redefinition we give here.

[4] To use the initial-value theorem (IVT) to find a TF, must have $\tilde{\phi}_\mathrm{s}(0) - \phi_\mathrm{sf}(0) = 0$, implying that $\bar{C}_\mathrm{dl}^\mathrm{sf}$ is initially charged to $U_\mathrm{ocp}(\theta_{\mathrm{s},0})$ and $i_\mathrm{dl}^\mathrm{sf}(0) = 0$, which causes $\eta(0) = 0$.

$$\bar{C}_{\mathrm{dl}}^{\mathrm{sf}}\frac{\partial(\phi_{\mathrm{s}}-\phi_{\mathrm{sf}})}{\partial t}=\bar{R}_{\mathrm{dl}}^{\mathrm{sf}}\bar{C}_{\mathrm{dl}}^{\mathrm{sf}}\frac{\partial i_{\mathrm{dl}}^{\mathrm{sf}}}{\partial t}+i_{\mathrm{dl}}^{\mathrm{sf}}$$

$$\bar{C}_{\mathrm{dl}}^{\mathrm{sf}}\frac{\partial(\tilde{\phi}_{\mathrm{s}}+U_{\mathrm{ocp}}(\theta_{\mathrm{s},0})-\phi_{\mathrm{sf}})}{\partial t}=\bar{R}_{\mathrm{dl}}^{\mathrm{sf}}\bar{C}_{\mathrm{dl}}^{\mathrm{sf}}\frac{\partial i_{\mathrm{dl}}^{\mathrm{sf}}}{\partial t}+i_{\mathrm{dl}}^{\mathrm{sf}}$$

$$s\bar{C}_{\mathrm{dl}}^{\mathrm{sf}}\left(\widetilde{\Phi}_{\mathrm{s}}(s)-\Phi_{\mathrm{sf}}(s)\right)=\left(s\bar{R}_{\mathrm{dl}}^{\mathrm{sf}}\bar{C}_{\mathrm{dl}}^{\mathrm{sf}}+1\right)I_{\mathrm{dl}}^{\mathrm{sf}}(s).$$

- Overall solid/film interface supports a total lithium flux:

$$I_{\mathrm{f+dl}}^{\mathrm{sf}}(s)=I_{\mathrm{f}}^{\mathrm{sf}}(s)+I_{\mathrm{dl}}^{\mathrm{sf}}(s)=\underbrace{\left(\frac{1}{\bar{R}_{\mathrm{ct}}^{\mathrm{sf}}+\bar{Z}_{\mathrm{s}}(s)}+\frac{s\bar{C}_{\mathrm{dl}}^{\mathrm{sf}}}{s\bar{R}_{\mathrm{dl}}^{\mathrm{sf}}\bar{C}_{\mathrm{dl}}^{\mathrm{sf}}+1}\right)}_{\bar{Y}_{\mathrm{sf}}(s)}\left(\widetilde{\Phi}_{\mathrm{s}}(s)-\Phi_{\mathrm{sf}}(s)\right),$$

  where $\bar{Y}_{\mathrm{sf}}(s)$ is overall admittance of interface and $\bar{Z}_{\mathrm{sf}}(s)=1/\bar{Y}_{\mathrm{sf}}(s)$.

Impedance at the film/electrolyte interface

- Now, we investigate the impedance at the film/electrolyte interface.
- Solve for $I_{\mathrm{f}}^{\mathrm{fe}}(s)$ by linearizing the Butler–Volmer equation for the interface and taking the Laplace transform of the result.
- At this interface, we ignore variation of OCP on concentration of lithium in film or in solution (same as Meyers, et al.).
- Following same method as before, we find (where $\bar{R}_{\mathrm{ct}}^{\mathrm{fe}}=RT/(i_0^{\mathrm{fe}}F)$):

$$\Phi_{\mathrm{fe}}-\Phi_{\mathrm{e}}=\bar{R}_{\mathrm{ct}}^{\mathrm{fe}}I_{\mathrm{f}}^{\mathrm{fe}}.$$

- The interface also supports a lithium flux due to the double layer:[5]

$$\bar{C}_{\mathrm{dl}}^{\mathrm{fe}}\frac{\partial(\phi_{\mathrm{fe}}-\phi_{\mathrm{e}})}{\partial t}=\bar{R}_{\mathrm{dl}}^{\mathrm{fe}}\bar{C}_{\mathrm{dl}}^{\mathrm{fe}}\frac{\partial i_{\mathrm{dl}}^{\mathrm{fe}}}{\partial t}+i_{\mathrm{dl}}^{\mathrm{fe}}$$

$$s\bar{C}_{\mathrm{dl}}^{\mathrm{fe}}\left(\Phi_{\mathrm{fe}}(s)-\Phi_{\mathrm{e}}(s)\right)=\left(s\bar{R}_{\mathrm{dl}}^{\mathrm{fe}}\bar{C}_{\mathrm{dl}}^{\mathrm{fe}}+1\right)I_{\mathrm{dl}}^{\mathrm{fe}}(s).$$

[5] To use IVT, $\bar{C}_{\mathrm{dl}}^{\mathrm{fe}}$ must be initially discharged to 0 V so that $\phi_{\mathrm{fe}}(0)-\phi_{\mathrm{e}}(0)=0$.

- Overall film/electrolyte interface supports a total lithium flux:

$$I^{\mathrm{fe}}_{\mathrm{f+dl}}(s) = I^{\mathrm{fe}}_{\mathrm{f}}(s) + I^{\mathrm{fe}}_{\mathrm{dl}}(s) = \underbrace{\left(\frac{1}{\bar{R}^{\mathrm{fe}}_{\mathrm{ct}}} + \frac{s\bar{C}^{\mathrm{fe}}_{\mathrm{dl}}}{s\bar{R}^{\mathrm{fe}}_{\mathrm{dl}}\bar{C}^{\mathrm{fe}}_{\mathrm{dl}} + 1} \right)}_{\bar{Y}_{\mathrm{fe}}(s)} \left(\Phi_{\mathrm{fe}}(s) - \Phi_{\mathrm{e}}(s) \right),$$

  where $\bar{Y}_{\mathrm{fe}}(s)$ is overall admittance of interface and $\bar{Z}_{\mathrm{fe}}(s) = 1/\bar{Y}_{\mathrm{fe}}(s)$.

Overall interfacial impedance model

- Finally, must add film resistance, and double layer between ϕ_{s} and ϕ_{e}.
- Start by recognizing that lithium flux $I^{\mathrm{sf}}_{\mathrm{f+dl}}(s)$ and $I^{\mathrm{fe}}_{\mathrm{f+dl}}(s)$ must be equal, and define that value to be $I^{\mathrm{f}}_{\mathrm{f+dl}}(s)$.
- Model resistance of film layer as purely ohmic:

$$\Phi_{\mathrm{sf}}(s) - \Phi_{\mathrm{fe}}(s) = \bar{R}_{\mathrm{f}} I^{\mathrm{f}}_{\mathrm{f+dl}}(s).$$

- Rearrange equations for $I^{\mathrm{sf}}_{\mathrm{f+dl}}(s)$ and $I^{\mathrm{fe}}_{\mathrm{f+dl}}(s)$ and lithium flux through film resistance

$$\widetilde{\Phi}_{\mathrm{s}}(s) - \Phi_{\mathrm{sf}}(s) = \bar{Z}_{\mathrm{sf}}(s) I^{\mathrm{f}}_{\mathrm{f+dl}}(s)$$

$$\Phi_{\mathrm{sf}}(s) - \Phi_{\mathrm{fe}}(s) = \bar{R}_{\mathrm{f}} I^{\mathrm{f}}_{\mathrm{f+dl}}(s)$$

$$\Phi_{\mathrm{fe}}(s) - \Phi_{\mathrm{e}}(s) = \bar{Z}_{\mathrm{fe}}(s) I^{\mathrm{f}}_{\mathrm{f+dl}}(s).$$

- Adding these three equations to each other, we find that:

$$\widetilde{\Phi}_{\mathrm{s}}(s) - \Phi_{\mathrm{e}}(s) = \left(\bar{Z}_{\mathrm{sf}}(s) + \bar{R}_{\mathrm{f}} + \bar{Z}_{\mathrm{fe}}(s) \right) I^{\mathrm{f}}_{\mathrm{f+dl}}(s).$$

- Interfacial impedance model is nearly complete: all that remains is to consider double layer between ϕ_{s} and ϕ_{e}:[6]

[6] To use IVT, $\bar{C}^{\mathrm{se}}_{\mathrm{dl}}$ must be initially charged to $U_{\mathrm{ocp}}(\theta_{\mathrm{s},0})$ volts so that $\tilde{\phi}_{\mathrm{s}}(0) - \phi_{\mathrm{e}}(0) = 0$.

$$\bar{C}_{\rm dl}^{\rm se}\frac{\partial(\phi_{\rm s}-\phi_{\rm e})}{\partial t}=\bar{R}_{\rm dl}^{\rm se}\bar{C}_{\rm dl}^{\rm se}\frac{\partial i_{\rm dl}^{\rm se}}{\partial t}+i_{\rm dl}^{\rm se}$$

$$\bar{C}_{\rm dl}^{\rm se}\frac{\partial(\tilde{\phi}_{\rm s}+U_{\rm ocp}(\theta_{\rm s,0})-\phi_{\rm e})}{\partial t}=\bar{R}_{\rm dl}^{\rm se}\bar{C}_{\rm dl}^{\rm se}\frac{\partial i_{\rm dl}^{\rm se}}{\partial t}+i_{\rm dl}^{\rm se}$$

$$s\bar{C}_{\rm dl}^{\rm se}\left(\widetilde{\Phi}_{\rm s}(s)-\Phi_{\rm e}(s)\right)=\left(s\bar{R}_{\rm dl}^{\rm se}\bar{C}_{\rm dl}^{\rm se}+1\right)I_{\rm dl}^{\rm se}(s).$$

- Total lithium flux from solid to electrolyte is $I_{\rm f+dl}^{\rm se}(s)=I_{\rm f+dl}^{\rm f}(s)+I_{\rm dl}^{\rm se}(s)$:

$$I_{\rm f+dl}^{\rm se}(s)=\left(\frac{1}{\bar{Z}_{\rm sf}(s)+\bar{R}_{\rm f}+\bar{Z}_{\rm fe}(s)}+\frac{s\bar{C}_{\rm dl}^{\rm se}}{s\bar{R}_{\rm dl}^{\rm se}\bar{C}_{\rm dl}^{\rm se}+1}\right)\left(\widetilde{\Phi}_{\rm s}(s)-\Phi_{\rm e}(s)\right).$$

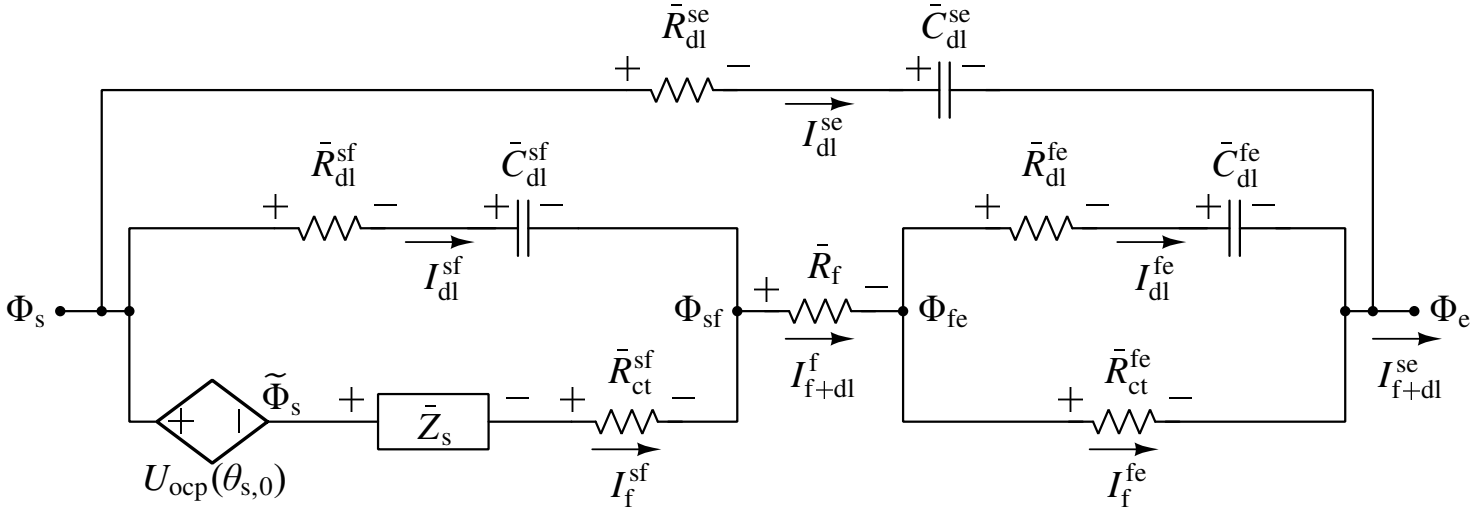
- Defining $\phi_{\rm s\text{-}e}=\phi_{\rm s}-\phi_{\rm e}$ and $\tilde{\phi}_{\rm s\text{-}e}=\tilde{\phi}_{\rm s}-\phi_{\rm e}$, we have now derived the impedance of the interface:

$$\frac{\widetilde{\Phi}_{\rm s\text{-}e}(s)}{I_{\rm f+dl}^{\rm se}(s)}=\bar{Z}_{\rm se}(s),$$

  where,

$$\bar{Z}_{\rm se}(s)=\left(\frac{1}{\bar{Z}_{\rm sf}(s)+\bar{R}_{\rm f}+\bar{Z}_{\rm fe}(s)}+\frac{s\bar{C}_{\rm dl}^{\rm se}}{s\bar{R}_{\rm dl}^{\rm se}\bar{C}_{\rm dl}^{\rm se}+1}\right)^{-1}.$$

- This interfacial model can be *visualized* using the equivalent circuit:[7]



[7] Note that the circuit was developed directly from the linearized model differential equations. The equations imply the circuit; the circuit does not define the model equations.

2.5: Upgrade 3: Adding double-layer CPE behavior

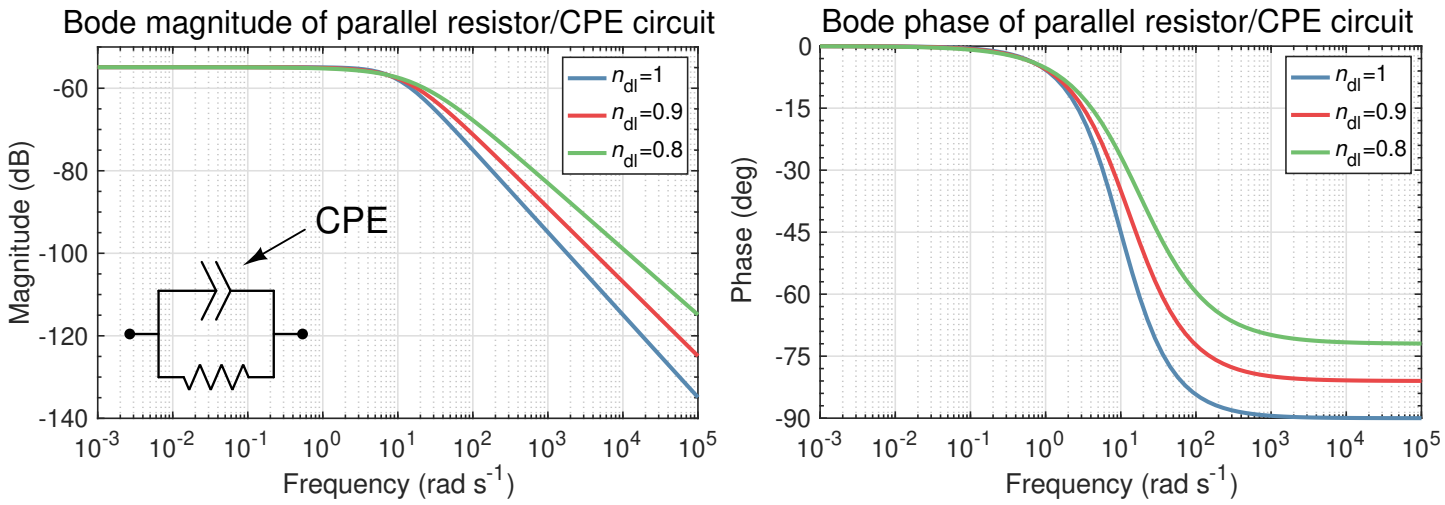
- Analysis so far in this chapter has focused on the solid/electrolyte interface for a single particle, not for an entire electrode.
- This ignores the inhomogeneous nature of physical electrodes; e.g.,
  - Variations in surface reactivity,
  - Variations in particle sizes, shapes, and surfaces of particles,
  - Fractal geometry of pore openings in electrode.
- When extending the interfacial model from particle-scale to a 1D continuum, these inhomogeneities are not always modeled well by the impedance $\bar{Z}_{\text{se}}(s)$ and its associated circuit found to date.
- But, by replacing ideal capacitances with constant-phase elements (CPEs) and by modifying particle impedance $\bar{Z}_{\text{s}}$, we can improve the ability of the interfacial model to describe observed behaviors.[8]

CPE due to distribution of particle sizes

- Distribution of particle size and shape in electrode causes impedance of overall double layer to differ from that of an ideal capacitance.
- Impedance of ideal capacitance is modeled as $Z_C(s) = 1/(s\bar{C})$.
- CPE replaces this impedance with $Z_{\tilde{C}}(s) = 1/(s^{n_{\text{dl}}}\bar{C})$, for $0 < n_{\text{dl}} \leq 1$.
- On a Bode plot, $Z_C(s)$ had a constant phase of -90° and $Z_{\tilde{C}}(s)$ has a constant phase of $-90^\circ \times n_{\text{dl}}$.
  - Both are CPEs, but new terminology used primarily when $n_{\text{dl}} \neq 1$.

[8] Jorcin, J.B., Orazem, M.E., Pébère, N., Tribollet, B., "CPE analysis by local electrochemical impedance spectroscopy," *Electrochimica Acta*, 51(8–9), 2006, 1473–9.

- Frequency response of resistor in parallel with CPE element:



- All model double-layer capacitances may easily be replaced by CPEs.
  - Simply replace s with s^n in capacitor impedances.
- We first rewrite $\bar{Z}_{\text{sf}}(s)$ and $\bar{Z}_{\text{fe}}(s)$ (notice that the tilde symbol ("~") in the subscript denotes a CPE):

$$\bar{Z}_{\tilde{\text{sf}}}(s) = \left(\frac{1}{\bar{R}_{\text{ct}}^{\text{sf}} + \bar{Z}_{\text{s}}(s)} + \frac{s^{n_{\text{dl}}^{\text{sf}}} \bar{C}_{\text{dl}}^{\text{sf}}}{s^{n_{\text{dl}}^{\text{sf}}} \bar{R}_{\text{dl}}^{\text{sf}} \bar{C}_{\text{dl}}^{\text{sf}} + 1} \right)^{-1}$$

$$\bar{Z}_{\tilde{\text{fe}}}(s) = \left(\frac{1}{\bar{R}_{\text{ct}}^{\text{fe}}} + \frac{s^{n_{\text{dl}}^{\text{fe}}} \bar{C}_{\text{dl}}^{\text{fe}}}{s^{n_{\text{dl}}^{\text{fe}}} \bar{R}_{\text{dl}}^{\text{fe}} \bar{C}_{\text{dl}}^{\text{fe}} + 1} \right)^{-1}.$$

- Using these new definitions, overall impedance may be rewritten:

$$\bar{Z}_{\tilde{\text{se}}}(s) = \left(\frac{1}{\bar{Z}_{\tilde{\text{sf}}}(s) + \bar{R}_{\text{f}} + \bar{Z}_{\tilde{\text{fe}}}(s)} + \frac{s^{n_{\text{dl}}^{\text{se}}} \bar{C}_{\text{dl}}^{\text{se}}}{s^{n_{\text{dl}}^{\text{se}}} \bar{R}_{\text{dl}}^{\text{se}} \bar{C}_{\text{dl}}^{\text{se}} + 1} \right)^{-1}.$$

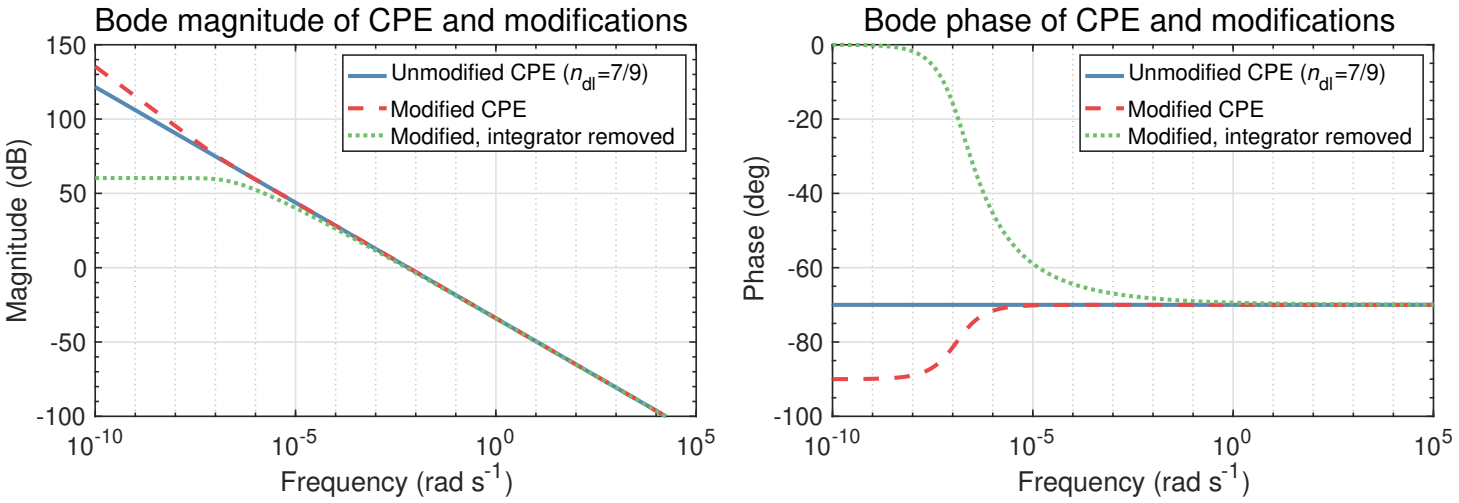
Modified CPE for double layer

- In Ch. 4, we face difficulties when using a pure double-layer CPE.
- To convert impedance models into ROMs, we must remove unstable dynamics as part of the process (then add them back in a later step).

- Double-layer CPE converts a pure integrator (the capacitor, which can be removed and re-added) into an element that can no longer be removed and re-added, breaking ROM-generation functions.
- So, we slightly modify our definition of $Z_{\widetilde{C}}$ (formerly, $Z_{\widetilde{C}} = 1/(s^{n_{\mathrm{dl}}}\bar{C})$).
- We desire to maintain consistent behavior for high frequencies, but to modify very low frequencies to get integration dynamics. Redefine:

$$Z_{\widetilde{C}}(s) = \frac{(s\bar{C} + \omega_{\mathrm{dl}})^{(1-n_{\mathrm{dl}})}}{s\bar{C}^{2-n_{\mathrm{dl}}}}.$$

- Comparing unmodified and modified $Z_{\widetilde{C}}(s)$ for $\omega_{\mathrm{dl}} = 1\ \mu\mathrm{Hz}$:[9]



- Note: Behaviors are changed only at very low frequencies, so for all reasonable frequencies this model approximates the CPE very well.
- Using these new definitions, overall impedance may be rewritten:

$$\bar{Z}_{\widetilde{\mathrm{se}}}(s) = \left(\frac{1}{\bar{Z}_{\widetilde{\mathrm{sf}}}(s) + \bar{R}_{\mathrm{f}} + \bar{Z}_{\widetilde{\mathrm{fe}}}(s)} + \frac{1}{\bar{R}^{\mathrm{se}}_{\mathrm{dl}} + Z^{\mathrm{se}}_{\widetilde{C}}(s)} \right)^{-1}.$$

[9] The integrator-removed version is $Z^{*}_{\widetilde{C}}(s) = Z_{\widetilde{C}}(s) - \left((\omega_{\mathrm{dl}})^{1-n_{\mathrm{dl}}} (\bar{C})^{n_{\mathrm{dl}}-2} \right)/s$.

2.6: Upgrades 4&5: Adding solid-diffusion CPE, SOC dependence

- The fractal nature of pore sizes and irregular particle shapes causes the solid-diffusion impedance also to have CPE-like behavior.
- This modifies the high-frequency portion of $\bar{Z}_\mathrm{s}$ (the low-frequency dynamics must remain unchanged, since the particles must integrate net lithium intercalated to account for a change in state-of-charge).
- We begin by recalling $\bar{Z}_\mathrm{s}(s)$ from before:

$$\bar{Z}_\mathrm{s}(s) = \underbrace{[U_\mathrm{ocp}]' \frac{|\theta_{100} - \theta_0|}{10\,800 \bar{D}_\mathrm{s} Q}}_{\text{constant}} \underbrace{\left[\frac{1}{1 - \sqrt{s/\bar{D}_\mathrm{s}} \coth\left(\sqrt{s/\bar{D}_\mathrm{s}}\right)} \right]}_{\text{dynamic}}.$$

- This impedance has a pole at $s = 0$ (not obvious by inspection), from which the integrator must be removed before applying the CPE.
- We examine the dynamic term inside the square brackets and compute the residue of the integrator pole to be:

$$\mathrm{res}_0 = \lim_{s \to 0} s \left[\frac{1}{1 - \sqrt{s/\bar{D}_\mathrm{s}} \coth\left(\sqrt{s/\bar{D}_\mathrm{s}}\right)} \right] = -3\bar{D}_\mathrm{s}.$$

- Integrator-removed portion of $\bar{Z}_\mathrm{s}(s)$ (i.e., $\bar{Z}^*_\mathrm{s}(s)$) can now be written as:

$$\begin{aligned} \bar{Z}^*_\mathrm{s}(s) &= [U_\mathrm{ocp}]' \frac{|\theta_{100} - \theta_0|}{10\,800 \bar{D}_\mathrm{s} Q} \left[\frac{1}{1 - \sqrt{s/\bar{D}_\mathrm{s}} \coth\left(\sqrt{s/\bar{D}_\mathrm{s}}\right)} - \frac{\mathrm{res}_0}{s} \right] \\ &= [U_\mathrm{ocp}]' \frac{|\theta_{100} - \theta_0|}{10\,800 \bar{D}_\mathrm{s} Q} \left[\frac{\left(s/\bar{D}_\mathrm{s}\right) + 3\left(1 - \sqrt{s/\bar{D}_\mathrm{s}} \coth\left(\sqrt{s/\bar{D}_\mathrm{s}}\right)\right)}{\left(s/\bar{D}_\mathrm{s}\right)\left(1 - \sqrt{s/\bar{D}_\mathrm{s}} \coth\left(\sqrt{s/\bar{D}_\mathrm{s}}\right)\right)} \right]. \end{aligned}$$

- Inside of $\bar{Z}^*_\mathrm{s}(s)$, we replace $\sqrt{s/\bar{D}_\mathrm{s}}$ with a constant-phase term:

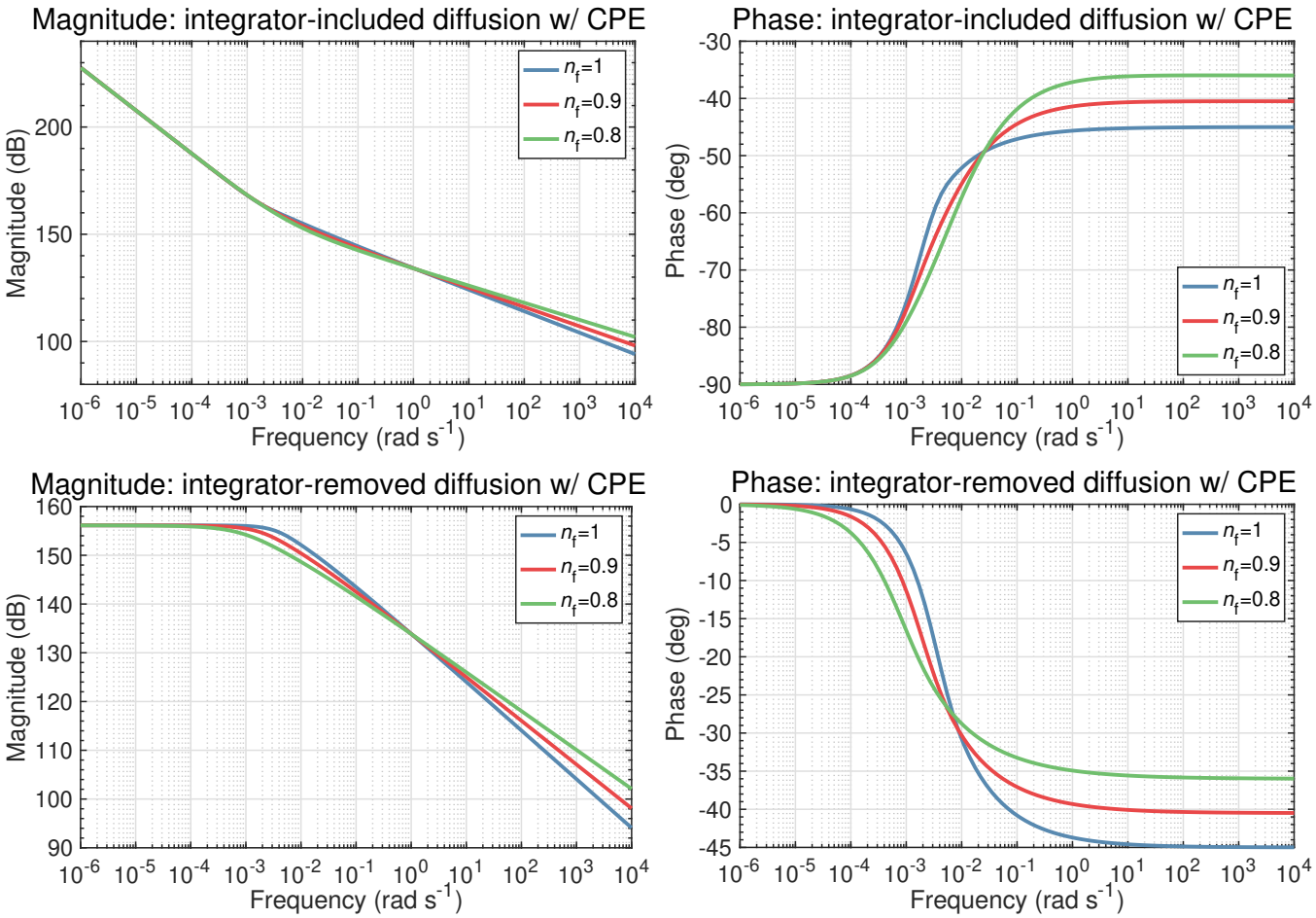
$$\beta_{\tilde{\mathrm{s}}}(s) = \sqrt{s^{n_\mathrm{f}}/\bar{D}_\mathrm{s}}.$$

- This results in integrator-removed and overall solid-diffusion impedances as:

$$\bar{Z}^{*}_{\tilde{s}}(s) = [U_{\text{ocp}}]' \frac{|\theta_{100} - \theta_0|}{10\,800 \bar{D}_{\text{s}} Q} \left[\frac{\beta^2_{\tilde{s}}(s) + 3\,(1 - \beta_{\tilde{s}}(s)\coth(\beta_{\tilde{s}}(s)))}{\beta^2_{\tilde{s}}(s)\,(1 - \beta_{\tilde{s}}(s)\coth(\beta_{\tilde{s}}(s)))} \right]$$

$$\bar{Z}_{\tilde{s}}(s) = [U_{\text{ocp}}]' \frac{|\theta_{100} - \theta_0|}{10\,800 \bar{D}_{\text{s}} Q} \left[\frac{\beta^2_{\tilde{s}}(s) + 3\,(1 - \beta_{\tilde{s}}(s)\coth(\beta_{\tilde{s}}(s)))}{\beta^2_{\tilde{s}}(s)\,(1 - \beta_{\tilde{s}}(s)\coth(\beta_{\tilde{s}}(s)))} - \frac{3\bar{D}_{\text{s}}}{s} \right].$$

- Example frequency response of diffusion impedance shown below.



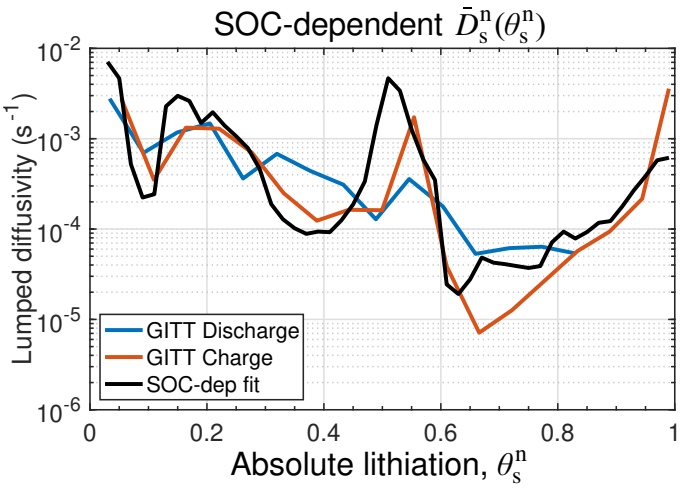
SOC-dependent solid diffusivity

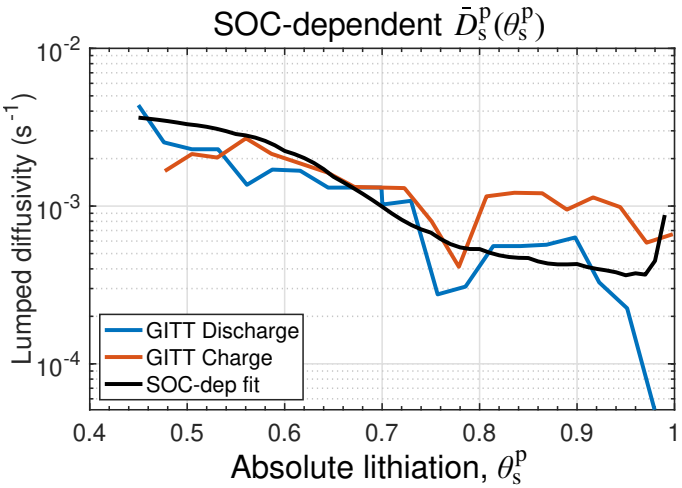
- When seeking to estimate parameter values for a commercial cell, using a constant $\bar{D}^{\text{r}}_{\text{s}}$ in each electrode does not fit observed data well.

- Here, we briefly mention a simple model of SOC-dependent solid diffusivity that improves solid-diffusion modeling significantly.[10]
- Definition of $\bar{D}_{\mathrm{s}}^{\mathrm{r}}$ is changed to:

$$\bar{D}_{\mathrm{s}}^{\mathrm{r}}\left(\theta_{\mathrm{s}}^{\mathrm{r}}\right) = \bar{D}_{\mathrm{s,ref}}^{\mathrm{r}} \underbrace{f\theta_{\mathrm{s}}^{\mathrm{r}}\left(\theta_{\mathrm{s}}^{\mathrm{r}}-1\right)\left[U_{\mathrm{ocp}}^{\mathrm{r}}\right]'}_{\text{SOC dependence}}.$$

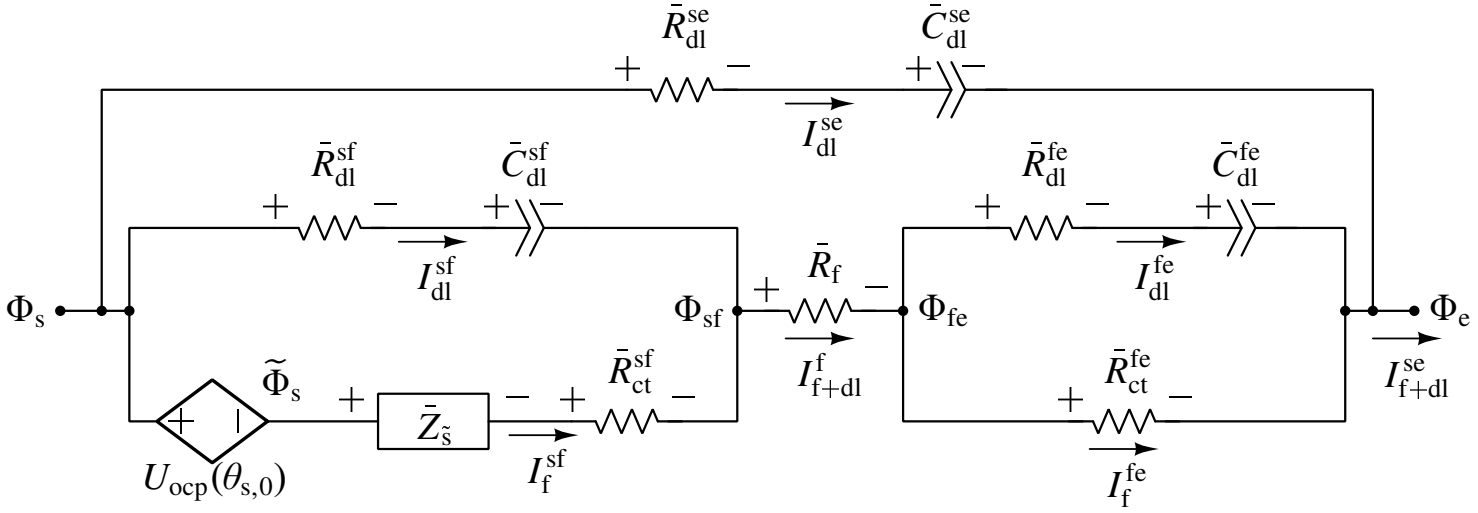
- The figures illustrate this relationship for constant $\bar{D}_{\mathrm{s,ref}}^{\mathrm{r}}$.





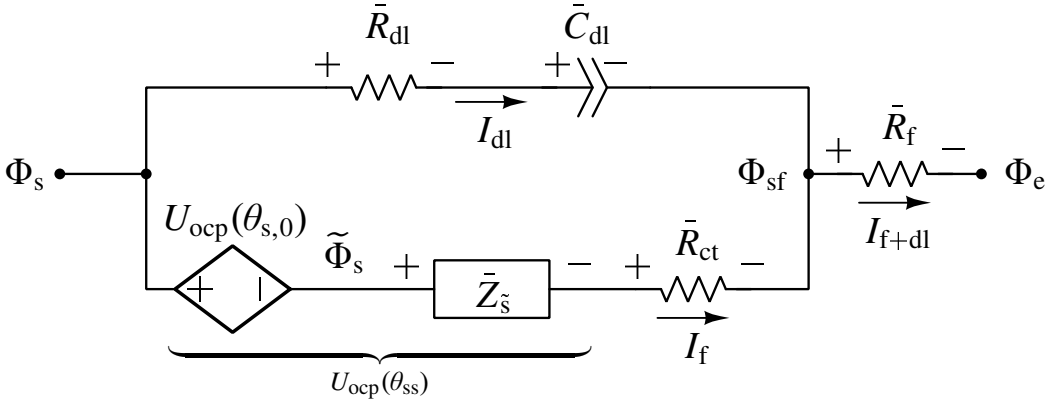
Summary of interfacial model

- The modified model can be *visualized* using the equivalent circuit:



[10] This model is developed in: Daniel R. Baker and Mark W. Verbrugge. Intercalate diffusion in multiphase electrode materials and application to lithiated graphite. *Journal of The Electrochemical Society*, 159(8):A1341, 2012.

- This interface model is more general than we are likely to need.
- In particular, it is difficult (impossible using practical equipment and measurements?) to identify all the model parameter values.
- Instead, we will use a simplified version (setting $\bar{R}_{\rm dl}^{\rm se} = \bar{R}_{\rm ct}^{\rm fe} = \bar{R}_{\rm dl}^{\rm fe} = 0$ and $\bar{C}_{\rm dl}^{\rm fe} = \bar{C}_{\rm dl}^{\rm se} = \infty$, and dropping some now-unneeded superscripts):



- For this model, $\bar{Z}_{\widetilde{\rm se}}(s) = \bar{Z}_{\widetilde{\rm sf}}(s) + \bar{R}_{\rm f}$, where:

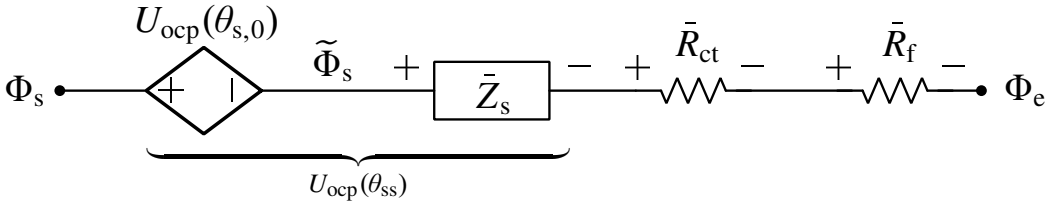
$$\bar{Z}_{\widetilde{\rm sf}}(s) = \left(\frac{1}{\bar{R}_{\rm ct} + \bar{Z}_{\tilde{\rm s}}(s)} + \frac{1}{\bar{R}_{\rm dl} + Z_{\widetilde{C}}(s)} \right)^{-1}$$

$$\bar{Z}_{\tilde{\rm s}}(s) = [U_{\rm ocp}]' \frac{|\theta_{100} - \theta_0|}{10\,800 \bar{D}_{\rm s} Q} \left[\frac{\beta_{\tilde{\rm s}}^2(s) + 3\left(1 - \beta_{\tilde{\rm s}}(s)\coth\left(\beta_{\tilde{\rm s}}(s)\right)\right)}{\beta_{\tilde{\rm s}}^2(s)\left(1 - \beta_{\tilde{\rm s}}(s)\coth\left(\beta_{\tilde{\rm s}}(s)\right)\right)} - \frac{3\bar{D}_{\rm s}}{s} \right]$$

$$Z_{\widetilde{C}}(s) = \frac{(s\bar{C}_{\rm dl} + \omega_{\rm dl})^{(1-n_{\rm dl})}}{s(\bar{C}_{\rm dl})^{2-n_{\rm dl}}}, \qquad \beta_{\tilde{\rm s}}(s) = \sqrt{s^{n_{\rm f}}/\bar{D}_{\rm s}}$$

$$\bar{i}_0 = \sum_{j=1}^{J} \bar{k}_{0,j} (X_j - x_{j,0})^{\omega_j(1-\alpha_j)} (x_{j,0})^{\omega_j \alpha_j}, \qquad \bar{R}_{\rm ct} = RT/(\bar{i}_0 F).$$

- Compare with the interface model we began with:



- Essentially the same, but now with inclusion of double layer and CPE.

Summary of modified PDEs

- Note: CPE behavior cannot be written as a standard time-domain PDE (fractional-order calculus is required, which is out of scope here).
  - The CPE behavior *can* be modeled perfectly in the Laplace domain for linearized transfer functions, which we do in Appendix 2.b.
  - Here, I recap the PDEs for non-CPE behaviors to show how the generalized double layer (simple model) changes them.
- The charge-conservation and mass conservation in electrolyte equations do not change.
- Must carefully distinguish i_f and $i_\mathrm{f+dl}$ in mass-conservation in solid.
- Solid mass conservation and kinetics add MSMR model details.

Charge conservation in the electrolyte:

- The PDE is: $$\frac{\partial}{\partial \tilde{x}}\left(\bar{\kappa}\left(\frac{\partial}{\partial \tilde{x}}\phi_\mathrm{e}+\bar{\kappa}_D T\frac{\partial \ln(\theta_\mathrm{e})}{\partial \tilde{x}}\right)\right)+i_\mathrm{f+dl}=0.$$
- The nonzero boundary conditions are:
$$-\bar{\kappa}\left[\frac{\partial}{\partial \tilde{x}}\phi_\mathrm{e}+\bar{\kappa}_D T\frac{\partial \ln(\theta_\mathrm{e})}{\partial \tilde{x}}\right]_{\tilde{x}=1,2}=i_\mathrm{app}.$$
- The initial condition is: $\phi_{\mathrm{e},0}=-U^\mathrm{n}_\mathrm{ocp}(\theta^\mathrm{n}_{\mathrm{s},0})$.

Mass conservation in the electrolyte:

- The PDE is: $$3600\bar{q}_\mathrm{e}\frac{\partial \theta_\mathrm{e}}{\partial t}=\bar{\psi}\frac{\partial}{\partial \tilde{x}}\bar{\kappa}\frac{\partial}{\partial \tilde{x}}\theta_\mathrm{e}+i_\mathrm{f+dl}.$$
- 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: $\theta_{\mathrm{e},0}=1$.

Charge conservation in the solid:

- The reformulated PDE is:

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

- The nonzero boundary conditions are:

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

- The initial value in the positive electrode is ($\phi^\mathrm{n}_{\mathrm{s},0} = 0$):

$$\phi^\mathrm{p}_{\mathrm{s},0} = U^\mathrm{p}_\mathrm{ocp}(\theta^\mathrm{p}_{\mathrm{s},0}) - U^\mathrm{n}_\mathrm{ocp}(\theta^\mathrm{n}_{\mathrm{s},0}).$$

Mass conservation in the solid:

- The PDE for $0 \le x_j \le X_j$ is (note that $\theta_\mathrm{s} = \sum_{j=1}^{J} x_j$ and $0 \le \theta_\mathrm{s} \le 1$):

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

- The nonzero boundary condition is (noting also that $i_\mathrm{f} = \sum_{j=1}^{J} i_{\mathrm{f},j}$):

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

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

$$x_{j,0} = \frac{X_j}{1+\exp\left[f(U_\mathrm{ocp}(\theta_{\mathrm{s},0}) - U^0_j)/\omega_j\right]}.$$

Kinetics: Note the distinct usage of $i_\mathrm{f+dl}$ versus i_f.

$$i_\mathrm{f} = \sum_{j=1}^{J} i_{\mathrm{f},j} = \sum_{j=1}^{J} i_{0,j}\left\{\exp\left((1-\alpha_j)f\eta\right) - \exp\left(-\alpha_j f\eta\right)\right\}$$

$$i_{0,j} = \bar{k}_{0,j}(X_j - x_{\mathrm{ss},j})^{\omega_j(1-\alpha_j)}(x_{\mathrm{ss},j})^{\omega_j\alpha_j}\,(\theta_\mathrm{e})^{1-\alpha_j}$$

$$\eta = \phi_\mathrm{s} - \phi_\mathrm{e} - U_\mathrm{ocp}(\theta_\mathrm{ss}) - \bar{R}_\mathrm{f} i_\mathrm{f+dl}.$$

- Notice that in the notation we use,

$$\bar{i}_{0,j} = \bar{k}_{0,j}(X_j - x_{j,0})^{\omega_j(1-\alpha_j)}(x_{j,0})^{\omega_j\alpha_j},$$

(where $\bar{i}_{0,j}$ has the overbar symbol) is a *constant* evaluated at some linearization setpoint while:

$$i_{0,j} = \bar{k}_{0,j}(X_j - x_{\mathrm{ss},j})^{\omega_j(1-\alpha_j)}(x_{\mathrm{ss},j})^{\omega_j\alpha_j}\,(\theta_\mathrm{e})^{1-\alpha_j},$$

(where $i_{0,j}$ does not have the overbar symbol) is a *time-varying* quantity that depends on the present local value of θ_e and $x_{\mathrm{ss},j}$.

- Finally, we must add a description of the double layer, which includes an equation to compute $i_{\mathrm{f+dl}}$ from i_f and i_dl.
- We need to be careful to note that the double layer spans ϕ_s to ϕ_sf, so an intermediate result is:

$$\bar{R}_\mathrm{dl}\bar{C}_\mathrm{dl}\frac{\partial i_\mathrm{dl}}{\partial t} + i_\mathrm{dl} = \bar{C}_\mathrm{dl}\frac{\partial\left(\phi_\mathrm{s} - \phi_\mathrm{sf}\right)}{\partial t}.$$

- We then recognize that $\phi_\mathrm{sf} = \phi_\mathrm{e} + \bar{R}_\mathrm{f} i_\mathrm{f+dl}$. Combining, we have:

Double layer:

$$\bar{R}_\mathrm{dl}\bar{C}_\mathrm{dl}\frac{\partial i_\mathrm{dl}}{\partial t} + i_\mathrm{dl} = \bar{C}_\mathrm{dl}\frac{\partial\left(\phi_\mathrm{s} - \phi_\mathrm{e} - \bar{R}_\mathrm{f} i_\mathrm{f+dl}\right)}{\partial t}$$

$$i_\mathrm{f+dl} = i_\mathrm{f} + i_\mathrm{dl}.$$

2.7: Seeking full-cell impedance model

- Cell impedance is dominated by solid/electrolyte interface impedance.
- So, we might consider simplifying via a single-particle model where:
  - Negative- and positive-electrode impedances are modeled as above using parameter values representative of each interface;
  - Electrolyte has additional ohmic resistance $\bar{R}_{\mathrm{e}}$ (includes separator).
- But, single-particle models may not be sufficient for the advanced physics-based BMS controls applications we will study later.
- So, we need to find a full-cell impedance model using all PDEs, not simply the solid-diffusion PDE.
- ECE5710 derived TFs from PDEs using two basic assumptions:[11]

  A1. Linearity: We linearized nonlinear equations using Taylor series;

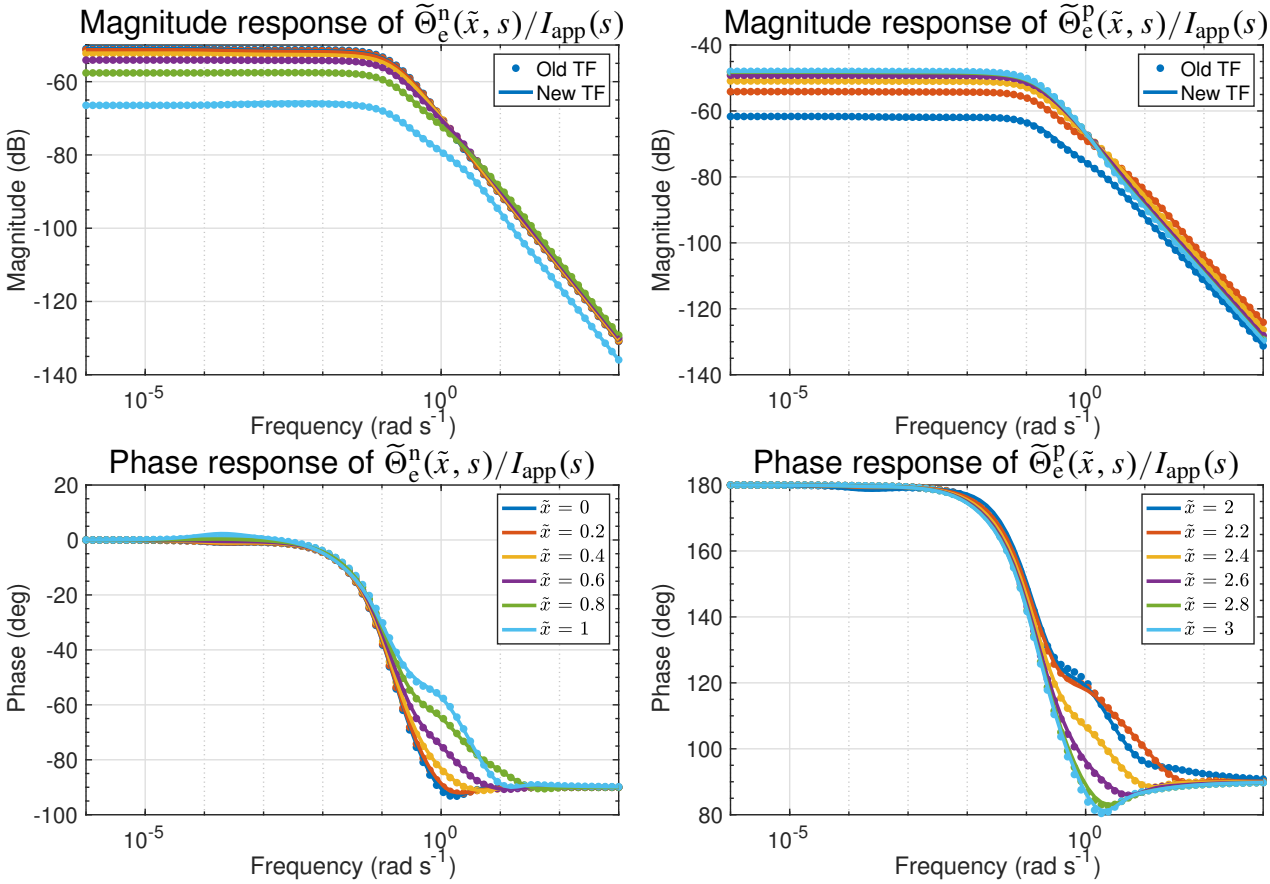
  A2. Assumed that reaction lithium flux $i_{\mathrm{f}}(x,t)$ was decoupled from (was not a function of) electrolyte concentration $\theta_{\mathrm{e}}(x,t)$.[12]
- These TFs can be combined to form a full-cell impedance model.
- Subsequent to introducing ECE5710, we found a different way to derive TFs that does not require making **A2** (cf. App. 2.b).
  - The new method works better for constant-current events since it does not ignore the coupling between $i_{\mathrm{f}}(x,t)$ and $\theta_{\mathrm{e}}(x,t)$.
- Example Bode plots shown here for parameter set listed in App. 2.f.
  - "Old" TFs were derived in ECE5710. A summary of these TFs, reformulated to use lumped parameters, is in App. 2.d.

[11] Simulations show that **A2** is quite good for HEV-type simulations (random, charge-neutral). **A1** is less good, but nonlinear corrections help improve linear predictions.

[12] In standard notation, $j(x,t)$ was assumed not to be a function of $c_{\mathrm{e}}(x,t)$.

- "New" TFs do not make assumption **A2**.

- Magnitude and phase responses for $\widetilde{\Theta}_{\mathrm{e}}(\tilde{x}, s)/I_{\mathrm{app}}(s)$ for different locations within the cell are shown below:[13]

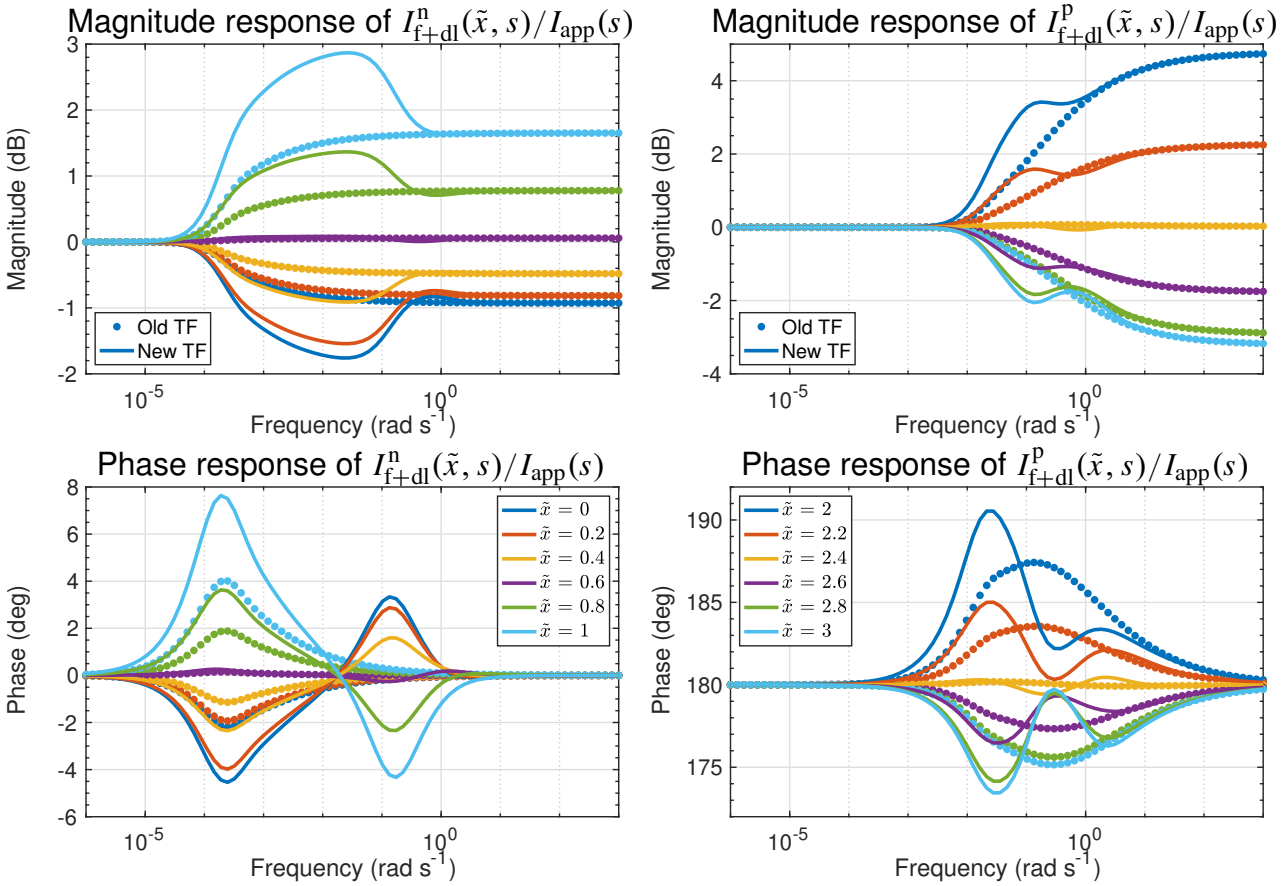


- For now, the interfacial model is still the simple model introduced in ECE5710, without double-layer capacitance.

- Notice that the frequency responses for this variable are almost identical for "old" and "new" transfer functions.
  - This explains, in part, why the "old" transfer functions worked well.
  - But, curiously, other transfer functions show greater differences, even though they are all computed directly from $\widetilde{\Theta}_{\mathrm{e}}(\tilde{x}, s)/I_{\mathrm{app}}(s)$.

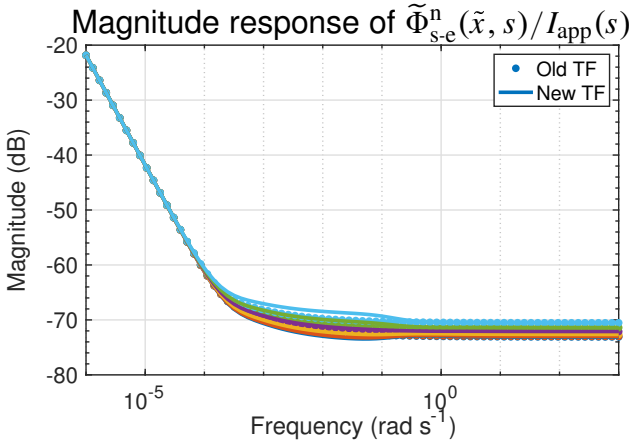
[13] If we know $c_{\mathrm{e},0}$, $\widetilde{C}_{\mathrm{e}}(\tilde{x}, s)/I_{\mathrm{app}}(s) = c_{\mathrm{e},0}\widetilde{\Theta}_{\mathrm{e}}(\tilde{x}, s)/I_{\mathrm{app}}(s)$.

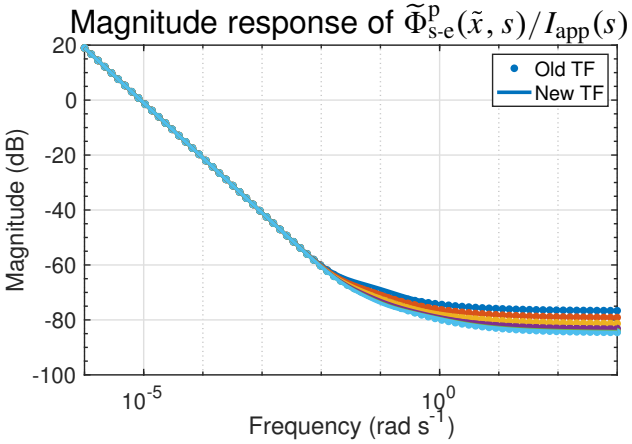
- The interfacial lithium flux frequency responses at different locations within the cell are (no double layer in this example so $i_{\text{dl}}^{\text{r}} = 0$):[14]

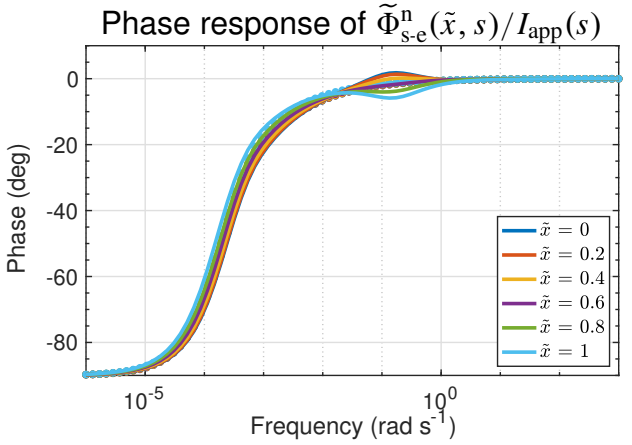


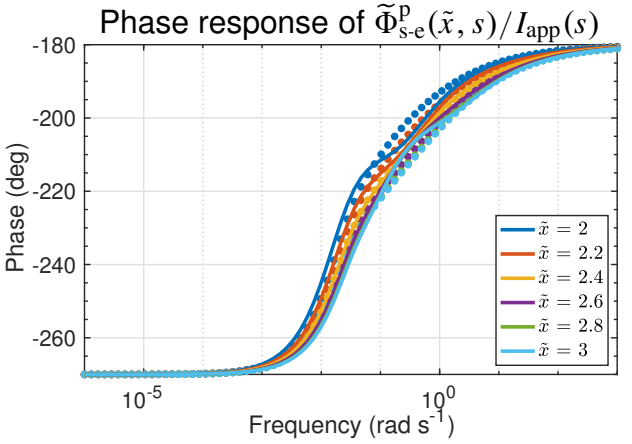
- Old and new TFs have identical dc and infinite-frequency values.
  - But, mid-frequency responses depend strongly on the effect of the gradient of θ_{e} on ϕ_{e}, which was previously ignored by **A2**.
- The phase-potential-difference frequency responses are shown next.
  - Low and high-frequency responses are unchanged, but intermediate frequencies have different responses.
- In Ch. 4, when studying time-domain simulation, we will need to compute "integrator-removed" TFs (recall: $[\cdot]^*$ denotes an integrator-removed TF).
- Integrator-removed phase-potential-difference results are also shown.

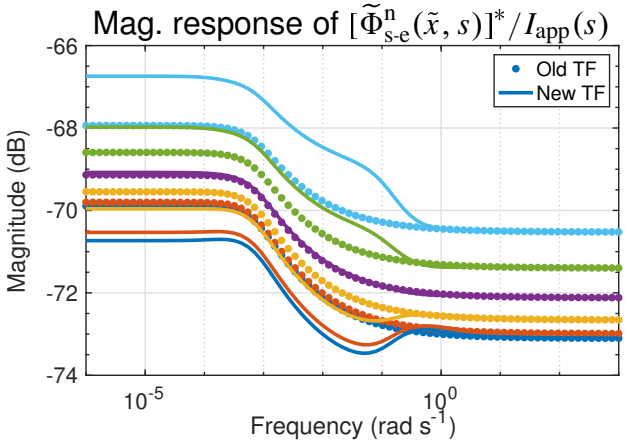
[14] If we know $\bar{j}$, we can also compute $J(\tilde{x}, s)/I_{\text{app}}(s) = (\bar{j}/F) I_{\text{f+dl}}(\tilde{x}, s)/I_{\text{app}}(s)$.

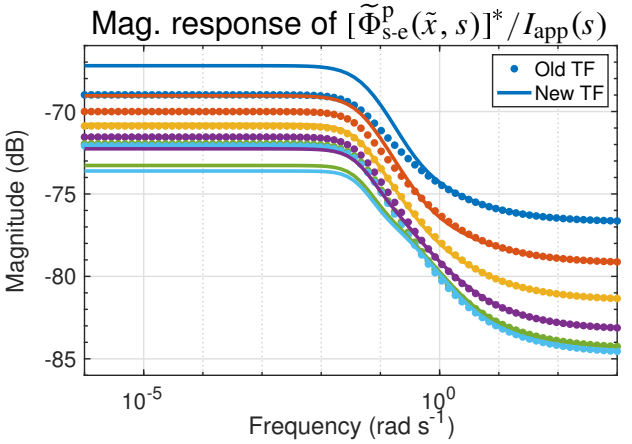


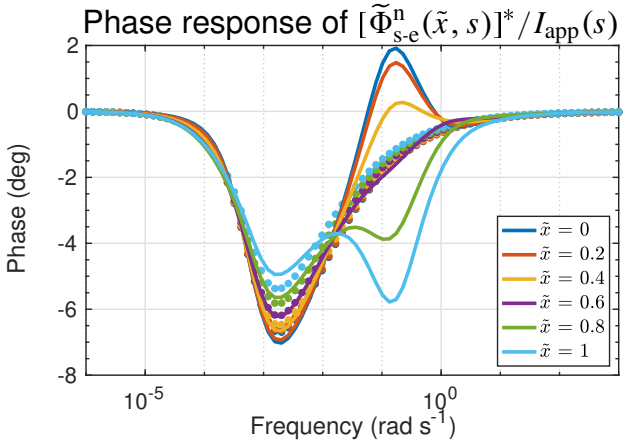


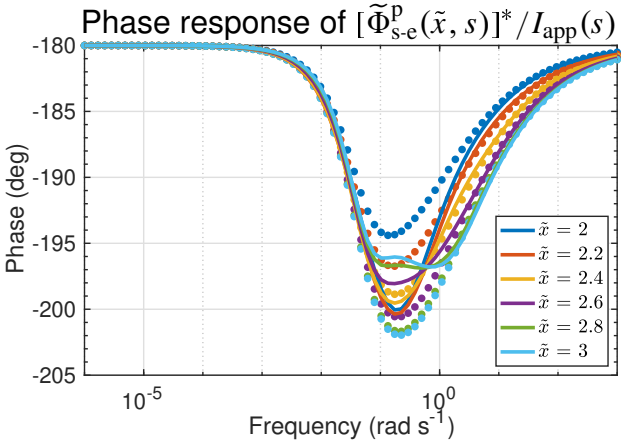




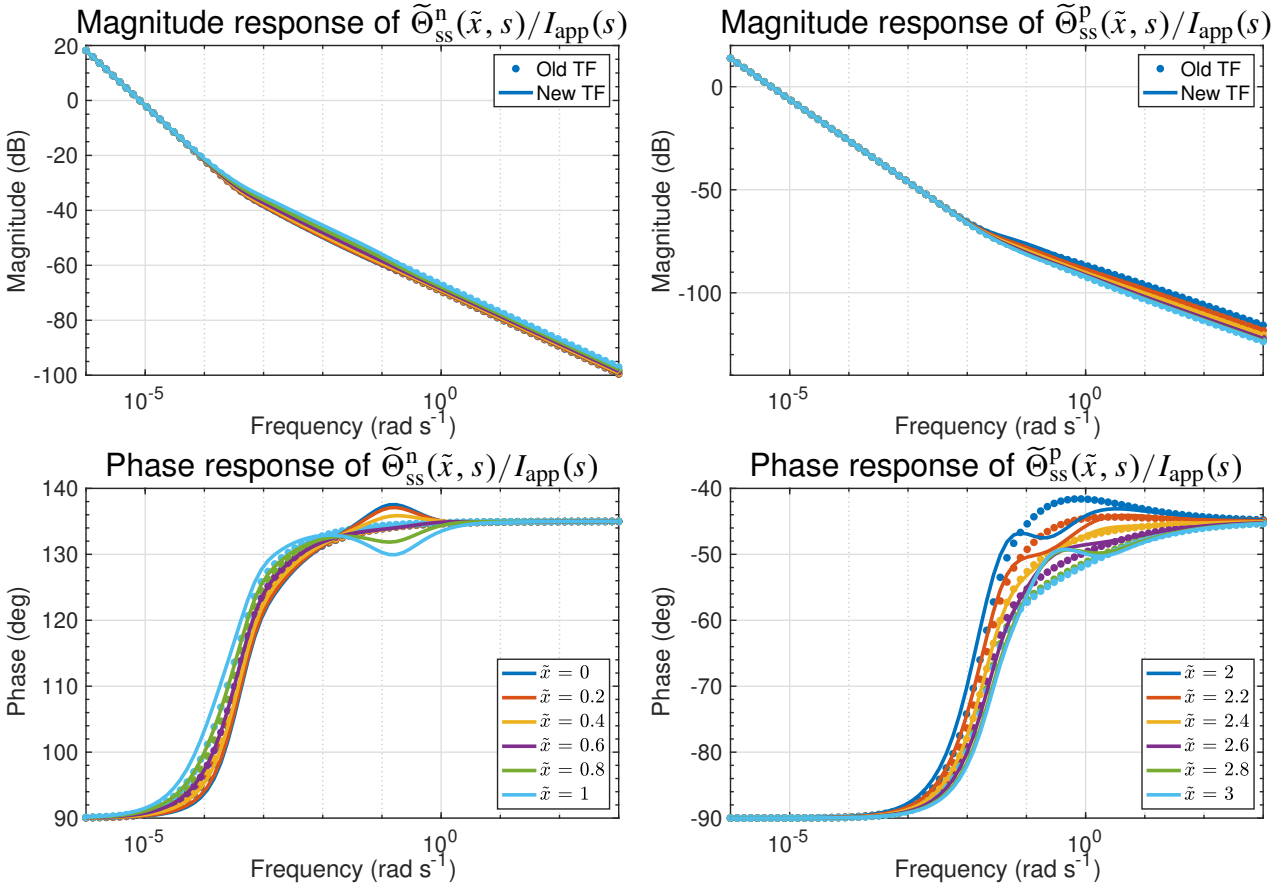




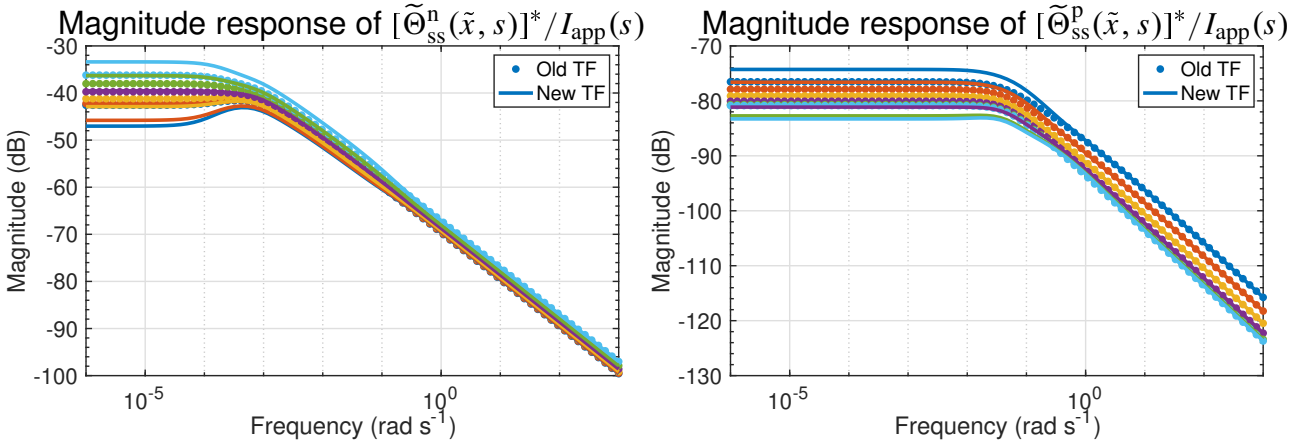




- In the latter case, dc and mid-frequency gain is affected by gradient in θ_e (previously ignored by **A2**), but limit as $s \to \infty$ is unchanged.
- The solid-surface-concentration frequency responses are:[15]

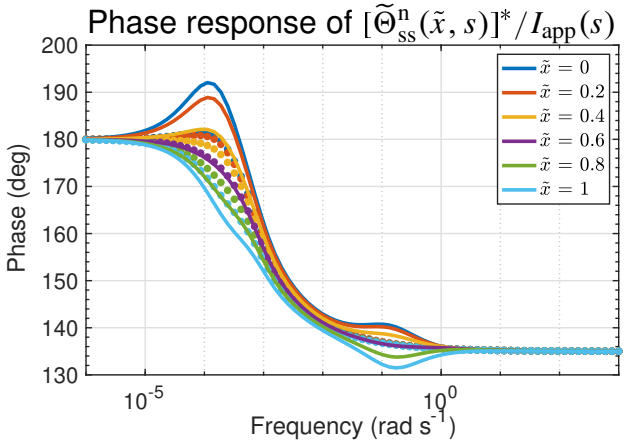


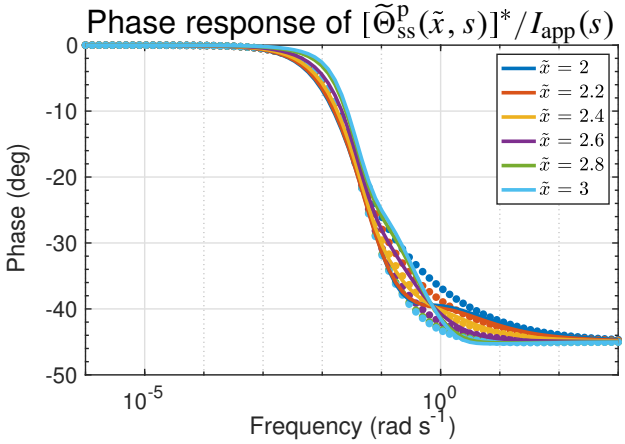
- Can remove the integrator from this variable to find (once again, $[\cdot]^*$ notation indicates that we have removed integrator term from TF):[16]



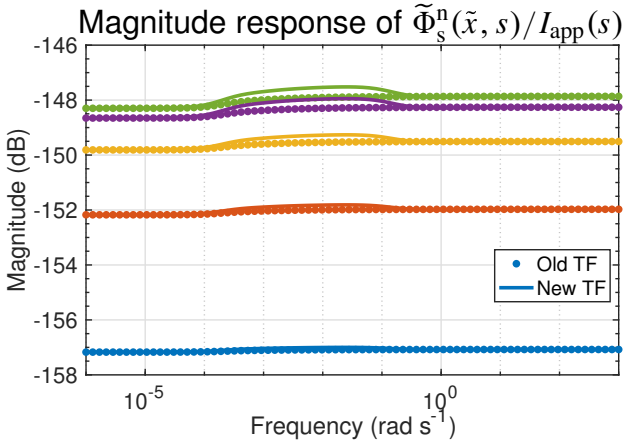
[15] Knowing $c_{s,max}$, we can also find $\widetilde{C}_{s,e}(\tilde{x},s)/I_{app}(s) = c_{s,max}\widetilde{\Theta}_{ss}(\tilde{x},s)/I_{app}(s)$.

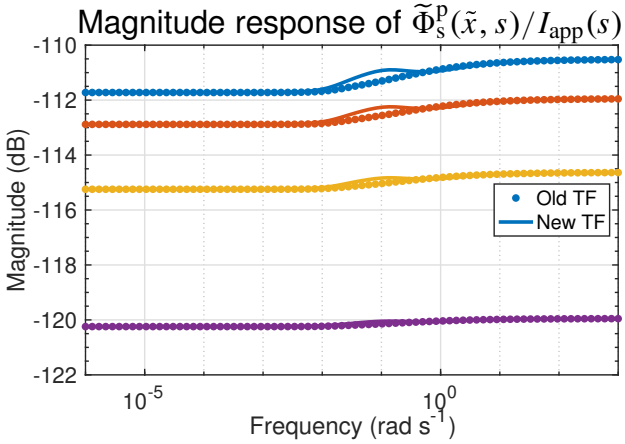
[16] Knowing $c_{s,max}$, we can also find $[\widetilde{C}_{s,e}(\tilde{x},s)]^*/I_{app}(s) = c_{s,max}[\widetilde{\Theta}_{ss}(\tilde{x},s)]^*/I_{app}(s)$.

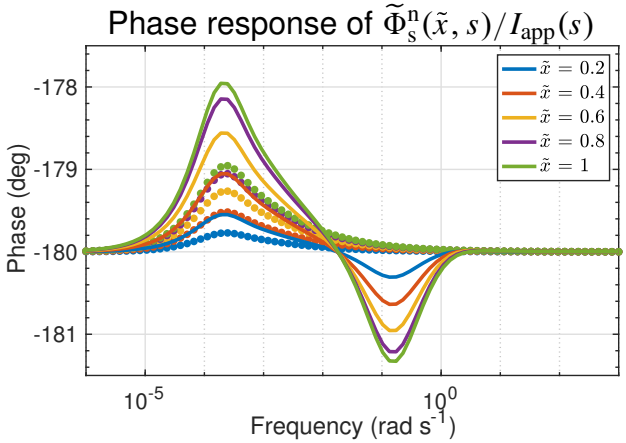


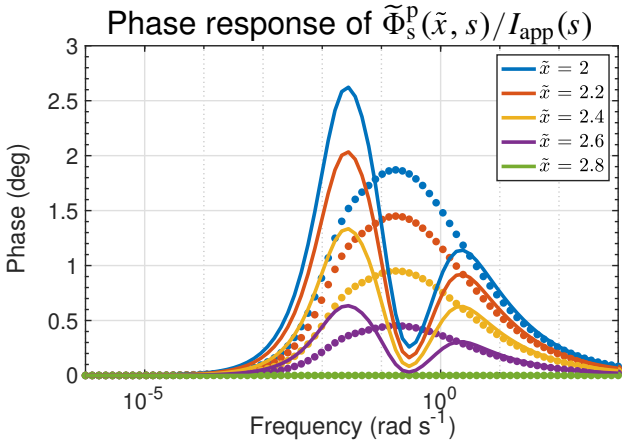


- Again, θ_{e} (or c_{e}) affects dc gain (ignored by assumption **A2**).
- The solid-potential frequency responses are:

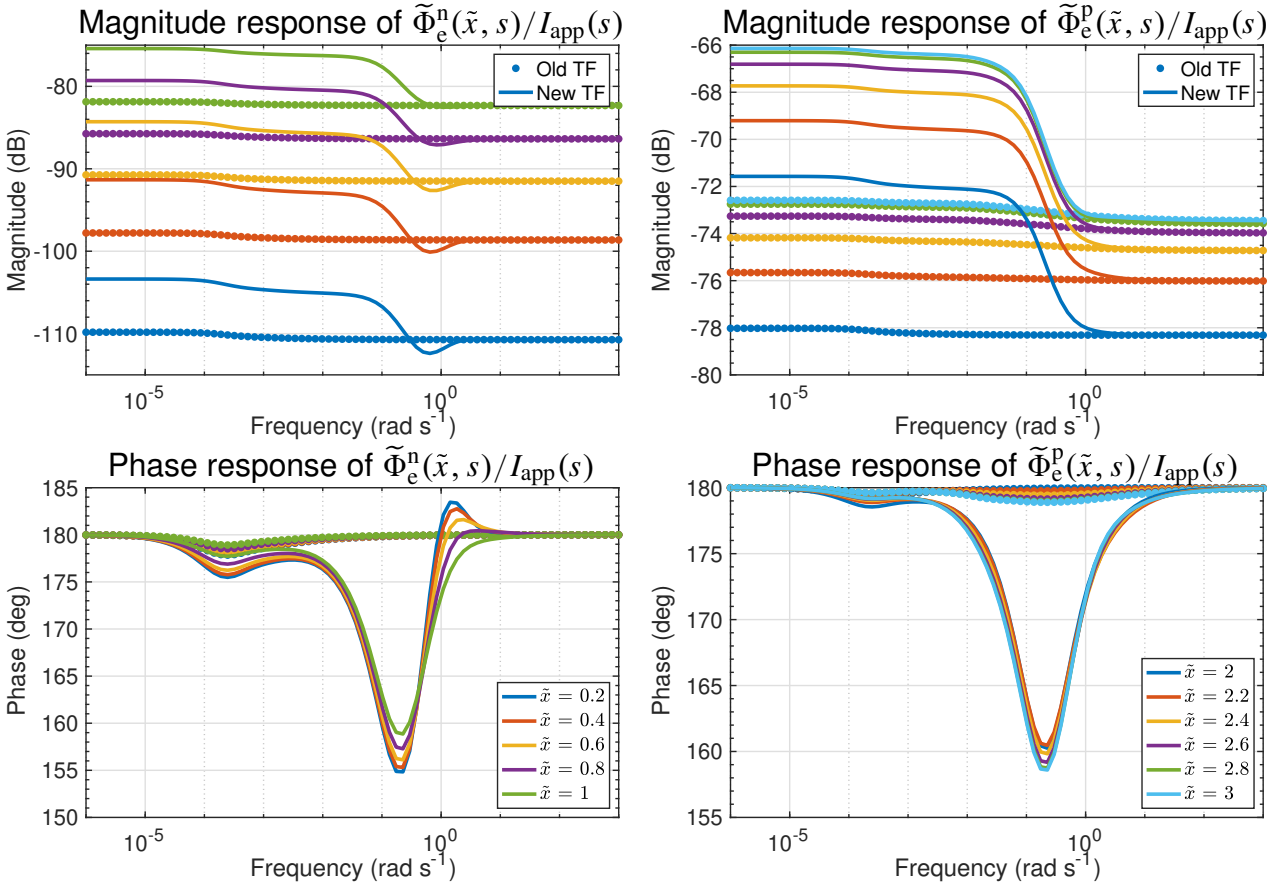








- In this case, dc and infinite-frequency gains have the same values for the old and new TFs but differ at intermediate frequencies.
- The electrolyte-potential frequency responses are:



- The "old" TFs include only $[\widetilde{\Phi}_{\mathrm{e}}(\tilde{x},s)]_1/I_{\mathrm{app}}(s)$ but the "new" TFs also include $[\widetilde{\Phi}_{\mathrm{e}}(\tilde{x},s)]_2/I_{\mathrm{app}}(s)$ in these plots.
- The dc gain strongly depends on the contribution of the electrolyte concentration (previously ignored by **A2**).
- Importantly, with this new approach we account for the dynamics that assumption **A2** was ignoring.

2.8: Full cell impedance response

- We are now ready to build a full-cell impedance model.
- In a laboratory, impedance is measured using electrochemical impedance spectroscopy (EIS).
- A small-magnitude sinusoidal input current (or voltage perturbation) is applied to a cell, and its voltage-perturbation (or current) response is monitored.
  - For example, $i_{\text{app}}(t) = M_1(\omega)\cos(\omega t + \phi_1(\omega))$.
- The procedure assumes that cell has linear response around present operating condition, uses small-magnitude input to ensure this.
- Therefore, (steady-state) output will also be sinusoidal of the same frequency, but having different magnitude and phase from the input.
  - For example, $\tilde{v}(t) = v(t) - \text{OCV} = M_2(\omega)\cos(\omega t + \phi_2(\omega))$.
- Magnitude response = ratio of output- to input-signal magnitude and phase response = difference between output and input phases:

$$M(\omega) = M_2(\omega)/M_1(\omega), \quad \text{and} \quad \phi(\omega) = \phi_2(\omega) - \phi_1(\omega).$$

- We will see that cell impedance is related to cell frequency response, which is $H(j\omega) = M(\omega)\exp(j\phi(\omega))$.
- The cell impedance can also be expressed using our TF models.
- Start with the voltage equation (using $\tilde{x}$ coordinates in electrodes):

$$v(t) = \phi_{\text{s}}^{\text{p}}(3,t) - \phi_{\text{s}}^{\text{n}}(0,t).$$

- Recall that our transfer functions compute $\tilde{\phi}_{\text{s}}^{\text{r}}$ and not $\phi_{\text{s}}^{\text{r}}$ directly.
- And, the biasing term is cell voltage itself in the positive electrode, so we cannot use the transfer functions for $\tilde{\phi}_{\text{s}}^{\text{r}}$ to find cell voltage.

- Instead, we write $\phi_{\rm s}^{\rm r} = \phi_{\rm s\text{-}e}^{\rm r} + \phi_{\rm e}^{\rm r}$, so (again using $\tilde{x}$ coordinates):

$$\begin{aligned} v(t) &= \left(\phi_{\rm s\text{-}e}^{\rm p}(3,t) + \phi_{\rm e}^{\rm p}(3,t)\right) - \left(\phi_{\rm s\text{-}e}^{\rm n}(0,t) + \phi_{\rm e}^{\rm n}(0,t)\right) \\ &= \left(\tilde{\phi}_{\rm s\text{-}e}^{\rm p}(3,t) + U_{\rm ocp}^{\rm p}(\theta_{\rm s,0}^{\rm p}) + \tilde{\phi}_{\rm e}^{\rm p}(3,t) + \phi_{\rm e}^{\rm n}(0,t)\right) \\ &\quad - \left(\tilde{\phi}_{\rm s\text{-}e}^{\rm n}(0,t) + U_{\rm ocp}^{\rm n}(\theta_{\rm s,0}^{\rm n}) + \tilde{\phi}_{\rm e}^{\rm n}(0,t) + \phi_{\rm e}^{\rm n}(0,t)\right). \end{aligned}$$

- Define debiased (linearized) voltage (where $\tilde{\phi}_{\rm e}^{\rm n}(0,t) = 0$):

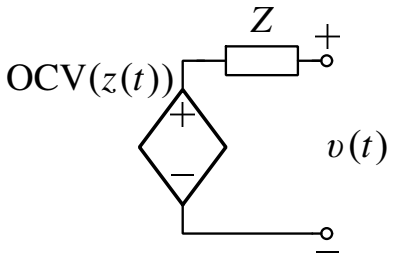
$$\begin{aligned} \tilde{v}(t) &= v(t) - \left(U_{\rm ocp}^{\rm p}(\theta_{\rm s,0}^{\rm p}) - U_{\rm ocp}^{\rm n}(\theta_{\rm s,0}^{\rm n})\right) \\ &= \left(\tilde{\phi}_{\rm s\text{-}e}^{\rm p}(3,t) + \tilde{\phi}_{\rm e}^{\rm p}(3,t)\right) - \left(\tilde{\phi}_{\rm s\text{-}e}^{\rm n}(0,t) + \tilde{\phi}_{\rm e}^{\rm n}(0,t)\right). \end{aligned}$$

- Then, can take Laplace transforms of $\tilde{v}(t)$ to find transfer function:

$$\frac{\widetilde{V}(s)}{I_{\rm app}(s)} = \frac{\widetilde{\Phi}_{\rm s\text{-}e}^{\rm p}(3,s)}{I_{\rm app}(s)} + \frac{\widetilde{\Phi}_{\rm e}^{\rm p}(3,s)}{I_{\rm app}(s)} - \frac{\widetilde{\Phi}_{\rm s\text{-}e}^{\rm n}(0,s)}{I_{\rm app}(s)}.$$

- Note that an impedance understanding of a cell writes:

$$\begin{aligned} v(t) &= \mathrm{OCV}(z(t)) - Z i_{\rm app}(t) \\ \tilde{v}(t) &= -Z i_{\rm app}(t) \\ \frac{\widetilde{V}(s)}{I_{\rm app}(s)} &= -Z(s). \end{aligned}$$



- So, can write overall cell impedance using TFs as:

$$Z(s) = -\left[\frac{\widetilde{\Phi}_{\rm s\text{-}e}^{\rm p}(3,s)}{I_{\rm app}(s)} + \frac{\widetilde{\Phi}_{\rm e}^{\rm p}(3,s)}{I_{\rm app}(s)} - \frac{\widetilde{\Phi}_{\rm s\text{-}e}^{\rm n}(0,s)}{I_{\rm app}(s)}\right].$$

- When applying this result, we need to be careful!
- In later chapters, we will find that we most frequently need to compute integrator-removed versions of $\widetilde{\Phi}_{\rm s\text{-}e}^{\rm r}(\tilde{x},s)/I_{\rm app}(s)$.

- If we are using integrator-removed TFs, need to add integrator term back before computing cell impedance. That is, we'll need to compute:

$$\frac{\widetilde{\Phi}^{\mathrm{r}}_{\mathrm{s\text{-}e}}(\tilde{x},s)}{I_{\mathrm{app}}(s)} = \left[\frac{\widetilde{\Phi}^{\mathrm{r}}_{\mathrm{s\text{-}e}}(\tilde{x},s)}{I_{\mathrm{app}}(s)}\right]^{*} + \frac{\mathrm{res}^{\mathrm{r}}_0}{s}$$

where, for this transfer function (cf. App. 2.e),

$$\mathrm{res}^{\mathrm{n}}_0 = \frac{\left|\theta^{\mathrm{n}}_{100} - \theta^{\mathrm{n}}_0\right| [U^{\mathrm{n}}_{\mathrm{ocp}}]'}{\bar{C}^{\mathrm{n}}_{\mathrm{dl}} \left|\theta^{\mathrm{n}}_{100} - \theta^{\mathrm{n}}_0\right| [U^{\mathrm{n}}_{\mathrm{ocp}}]' - 3600Q}$$

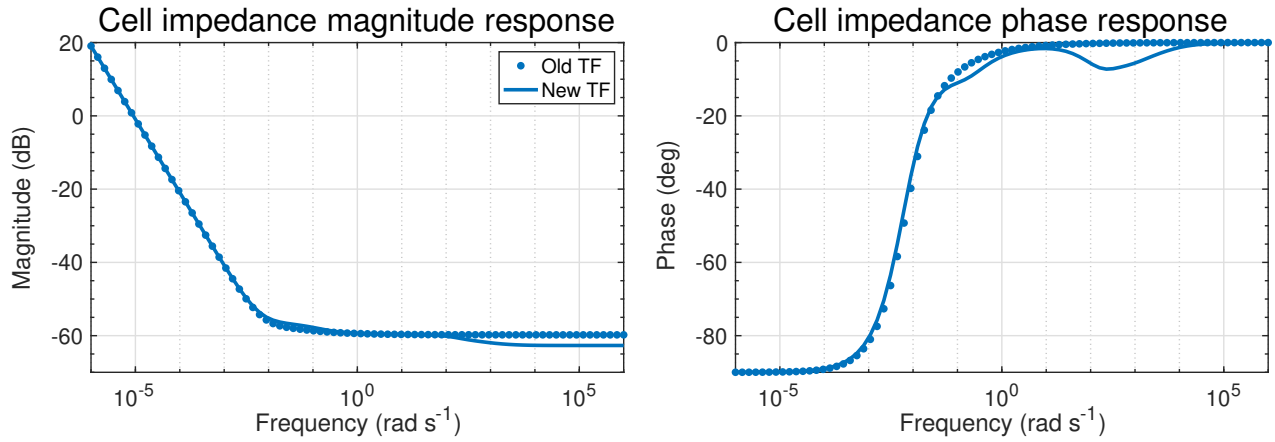
$$\mathrm{res}^{\mathrm{p}}_0 = \frac{-\left|\theta^{\mathrm{p}}_{100} - \theta^{\mathrm{p}}_0\right| [U^{\mathrm{p}}_{\mathrm{ocp}}]'}{\bar{C}^{\mathrm{p}}_{\mathrm{dl}} \left|\theta^{\mathrm{p}}_{100} - \theta^{\mathrm{p}}_0\right| [U^{\mathrm{p}}_{\mathrm{ocp}}]' - 3600Q}.$$

- Overall, using integrator-removed transfer functions,

$$Z(s) = -\left[\left[\frac{\widetilde{\Phi}^{\mathrm{p}}_{\mathrm{s\text{-}e}}(3,s)}{I_{\mathrm{app}}(s)}\right]^{*} + \frac{\widetilde{\Phi}^{\mathrm{p}}_{\mathrm{e}}(3,s)}{I_{\mathrm{app}}(s)} - \left[\frac{\widetilde{\Phi}^{\mathrm{n}}_{\mathrm{s\text{-}e}}(0,s)}{I_{\mathrm{app}}(s)}\right]^{*} + \frac{\mathrm{res}^{\mathrm{p}}_0 - \mathrm{res}^{\mathrm{n}}_0}{s}\right].$$

  - Of course, $Z(j\omega) = Z(s)|_{s=j\omega}$.

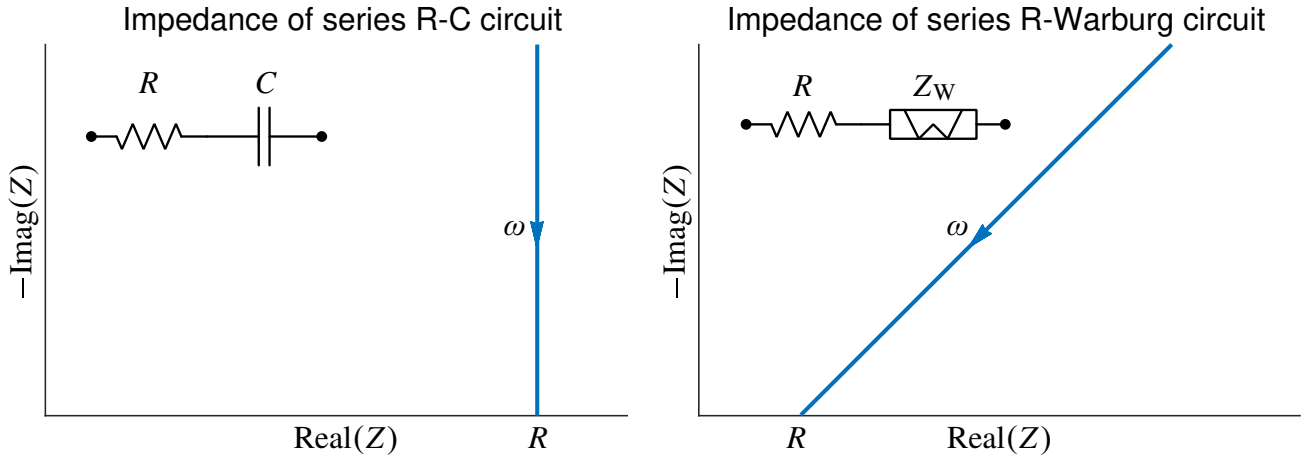
- Using this result, we can compute the impedance response of the cell using new and old transfer functions.



- In this case, the "New TF" has a double layer whereas the "Old TF" does not.
  - This accounts for most of the differences between the impedances.

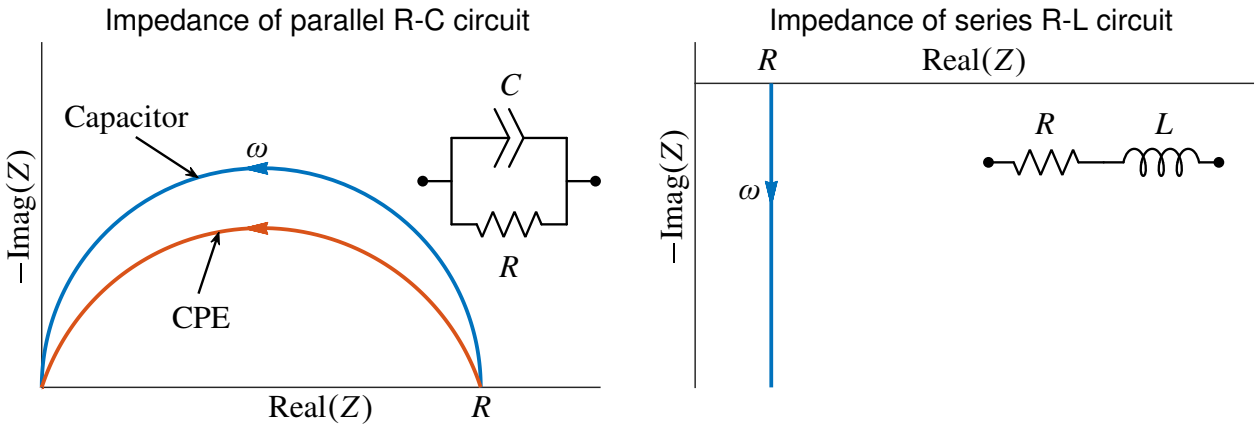
2.9: Nyquist (Cole–Cole) plots

- Bode plots aren't very helpful for visualizing an impedance response.
  - Not easy to see features of interest.
- We will find it more helpful to display Nyquist-style plots.
- A standard Nyquist plot is a parametric plot (versus frequency) that displays the real value of impedance on the horizontal axis and the imaginary value on the vertical axis.
  - This results in diagrams where most of the detail of interest is in the fourth quadrant, which is a little awkward.
  - Instead, we will plot real value vs. the *negative* of imaginary value.
    - In MATLAB: `plot(real(Z),-imag(Z));`
  - Results in diagrams where the detail of interest is in first quadrant.
- Even though this is not a standard Nyquist plot (because of the flipped vertical axis), we will still refer to it as a Nyquist plot.
- Nyquist plots take a little getting used to! Let's start by looking at Nyquist plots of some simple circuits.

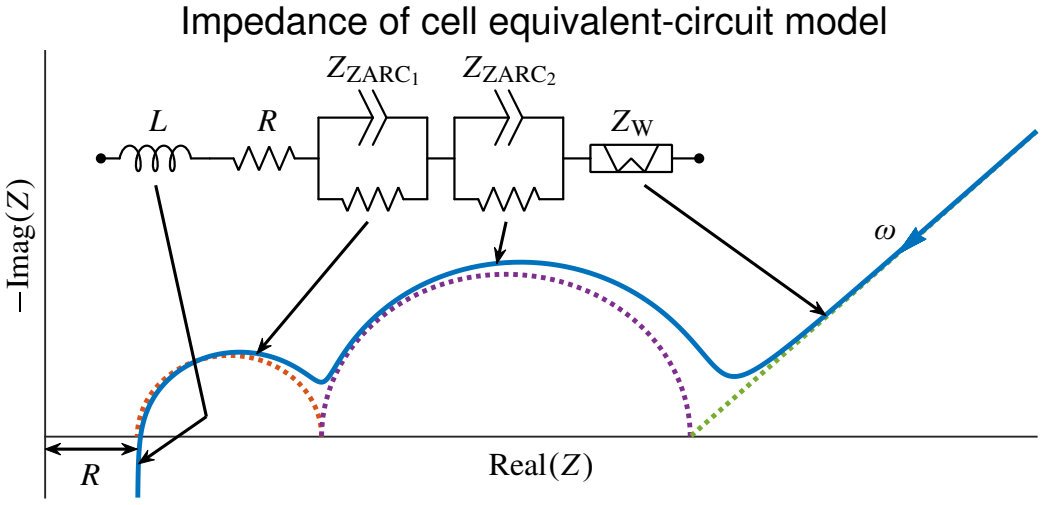


- The Nyquist plot of a capacitor's impedance ($Z_C = (j\omega C)^{-1}$) is a vertical line that approaches infinity at low frequencies.

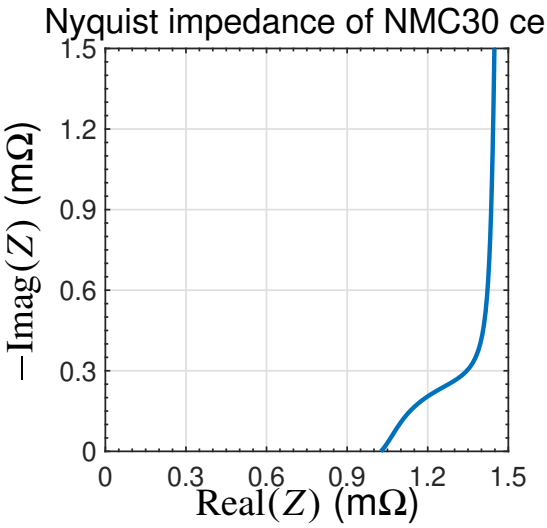
- Plot for series R–C circuit is shifted by R since $Z = R + (j\omega C)^{-1}$.
- The Nyquist plot of a Warburg impedance ($Z_W = W/\sqrt{j\omega}$) is a $45°$ line ending at the origin.
  - Series R–W circuit is shifted by R since $Z = R + W/\sqrt{j\omega}$.
  - Note that the Warburg impedance is a CPE with phase of $45°$.
- Plots for parallel R–C circuit and R–CPE (known as a ZARC element) below and to left; plot of series R–L circuit below and right.

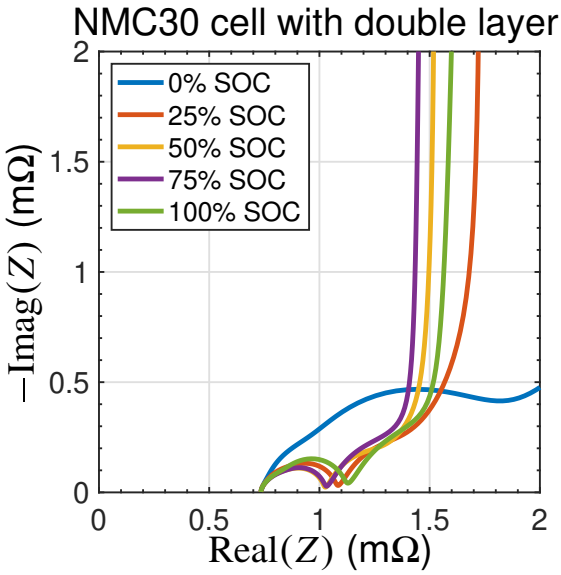


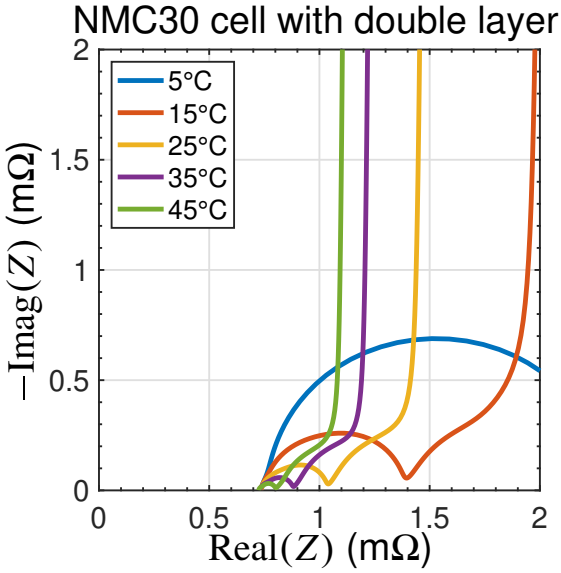
- Since impedances in series add, can visualize Nyquist diagrams for simple circuits by adding together simple responses.
- For example, a commonly seen cell equivalent-circuit model has Nyquist diagram:



- DFN model for NMC30 cell, with double-layer removed, has impedance as shown.
- It doesn't look a lot like the cartoon drawing, above.
- Reason: No double layer.
- But, new TFs can implement double-layer impedance.
- We restore double-layer parameters to NMC30 cell and plot cell-impedance Nyquist plots for different SOC values.
- The double-layer "bump" is now clearly visible.
- Also clear that impedance is a function of cell SOC.
- Reset SOC to 80% but change temperature: see that cell impedance varies significantly.
- All of these facts give us hope that testing a cell at different SOC values and different temperatures will help identify model parameter values.



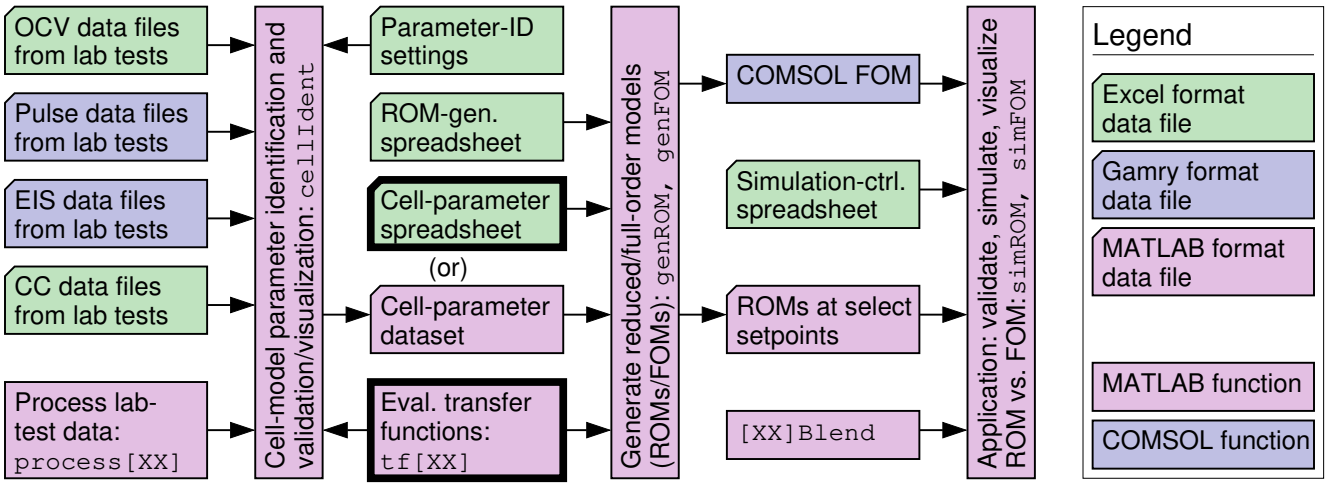




2.10: MATLAB toolbox

- It is very difficult to implement the TFs correctly (lots of details).
- So, we are providing MATLAB toolbox of verified functions.

Lithium-ion toolbox functions for parameter estimation and model simulation



- Most of the functionality of this toolbox has not been discussed yet.
  - The most critical parts for now are highlighted "Cell-parameter spreadsheet" and "Transfer functions" `tf[XX]` components.
- Parameter values are stored in custom-format Excel spreadsheets.

See *Instructions* tab for more information

Parameter	Code Name	Value		Unit
Cell name	name	Doyle		n/a
Standard variables (0) or lumped variables (1)	lumped	1		n/a

Cell Parameters

Parameter	Code Name	Value	Eact [kJ mol^{-1}]	Unit
Cell total capacity	Q	20.53599186	0	Ah
Electrolyte diffusivity / electrolyte conductivity	psi	2.23E-06	10	mol S^{-1} s^{-1}
kappa D	kD	-4.39E-04	0	V K^{-1}

Negative Electrode Parameters

Parameter	Code Name	Value	Eact [kJ mol^{-1}]	Unit
OCP as function of Stoichiometry	Uocp	@(x) (-0.16+1.32*exp(-3*x)+10*exp(-2000*x))	0	V
dOCP as function of Stoichiometry	dUocp	@(x) (-3.96*exp(-3*x)-20000*exp(-2000*x))	0	V
Electrode Stoichiometry at 0% SOC	theta0	0.0482	0	unitless
Electrode Stoichiometry at 100% SOC	theta100	0.5298	0	unitless
Lumped Solid Phase Conductivity	sigma	367968.75	0	S
Lumped Electrolyte Phase Conductivity	kappa	175.6521893	20	S
Solid-phase diffusivity CPE factor	nF	1	0	unitless

- Spreadsheet has sections for cell information, as well as for parameter values that apply over the whole cell, or only to negative-electrode, separator, or positive-electrode regions.

- Toolbox works both with standard parameter names and values and with lumped parameter names and values.
  - Simply replace “lumped” with 0 for standard parameters.
- MATLAB code `loadCellParams.m` loads spreadsheet into workspace:

```
>> cellParams = loadCellParams('cellDoyle.xlsx')

cellParams =

  struct with fields:

       const: [1x1 struct]
    function: [1x1 struct]
      lumped: 1
        name: 'Doyle'
```

- Every parameter value in the spreadsheet may be either a constant, or a function, or a lookup table.
- They are stored internally as functions of electrode stoichiometry `x` and temperature `T` in MATLAB:

```
>> cellParams.function.neg

ans =

  struct with fields:

        Uocp: @(x,T)(-0.16+1.32*exp(-3*x)+10*exp(-2000*x))
       dUocp: @(x,T)(-3.96*exp(-3*x)-20000*exp(-2000*x))
      theta0: @(x,T)(0.05)
    theta100: @(x,T)(0.53)
       sigma: @(x,T)(367969)
       kappa: @(x,T)(175.622*exp(20000/8.314*(1/298.15-1/T)))
          nf: @(x,T)(0.7)
          Ds: @(x,T)(0.0002496*exp(4000/8.314*(1/298.15-1/T)))
       Ea_Ds: @(x,T)(4000)
          ne: @(x,T)(0.143473)
```



```
          k0: @(x,T)(31.9637*exp(30000/8.314*(1/298.15-1/T)))
       Ea_k0: @(x,T)(30000)
          Rf: @(x,T)(0)
       alpha: @(x,T)(0.5)
         Cdl: @(x,T)(200)
         ndl: @(x,T)(1)
        wCdl: @(x,T)(6.2832e-05)
         Rdl: @(x,T)(0.001)
         soc: @(x,T)(0.05+x*(0.53-0.05))
```

- To convert the generic functions of SOC and temperature to a specific operational setpoint (and precompute common transfer-function terms at the frequency vector `s`), use `evalSetpoint.m`:

```
>> cellData = evalSetpoint(cellParams,s,0.5,25+273.15)

cellData =

  struct with fields:

       const: [1x1 struct]
    function: [1x1 struct]
      lumped: 1
        name: 'Doyle'
         neg: [1x1 struct]
         sep: [1x1 struct]
         pos: [1x1 struct]
      common: [1x1 struct]
```

- Functions are provided for the ten transfer functions
  - `tfIfdl.m` implements $I^{\mathrm{r}}_{\mathrm{f+dl}}(\tilde{x},s)/I_{\mathrm{app}}(s)$ for $\mathrm{r}\in\{\mathrm{n},\mathrm{p}\}$.
  - `tfIf.m` implements $I^{\mathrm{r}}_{\mathrm{f}}(\tilde{x},s)/I_{\mathrm{app}}(s)$ for $\mathrm{r}\in\{\mathrm{n},\mathrm{p}\}$.
  - `tfIdl.m` implements $I^{\mathrm{r}}_{\mathrm{dl}}(\tilde{x},s)/I_{\mathrm{app}}(s)$ for $\mathrm{r}\in\{\mathrm{n},\mathrm{p}\}$.
  - `tfPhie.m` implements $\widetilde{\Phi}^{\mathrm{r}}_{\mathrm{e}}(\tilde{x},s)/I_{\mathrm{app}}(s)$ for $\mathrm{r}\in\{\mathrm{n},\mathrm{s},\mathrm{p}\}$.
  - `tfPhis.m` implements $\widetilde{\Phi}^{\mathrm{r}}_{\mathrm{s}}(\tilde{x},s)/I_{\mathrm{app}}(s)$ for $\mathrm{r}\in\{\mathrm{n},\mathrm{p}\}$.
  - `tfPhiseInt.m` implements $\widetilde{\Phi}^{\mathrm{r}}_{\mathrm{s\text{-}e}}(\tilde{x},s)/I_{\mathrm{app}}(s)$ for $\mathrm{r}\in\{\mathrm{n},\mathrm{p}\}$.

- `tfPhise.m` implements $[\widetilde{\Phi}^{\mathrm{r}}_{\mathrm{s\text{-}e}}(\tilde{x},s)]^*/I_{\mathrm{app}}(s)$ for $\mathrm{r}\in\{\mathrm{n},\mathrm{p}\}$.
- `tfThetae.m` implements $\widetilde{\Theta}^{\mathrm{r}}_{\mathrm{e}}(\tilde{x},s)/I_{\mathrm{app}}(s)$ for $\mathrm{r}\in\{\mathrm{n},\mathrm{s},\mathrm{p}\}$.
- `tfThetassInt.m` implements $\widetilde{\Theta}^{\mathrm{r}}_{\mathrm{ss}}(\tilde{x},s)/I_{\mathrm{app}}(s)$ for $\mathrm{r}\in\{\mathrm{n},\mathrm{p}\}$.
- `tfThetass.m` implements $[\widetilde{\Theta}^{\mathrm{r}}_{\mathrm{ss}}(\tilde{x},s)]^*/I_{\mathrm{app}}(s)$ for $\mathrm{r}\in\{\mathrm{n},\mathrm{p}\}$.

- All of these transfer functions have same format. For example,

```
function [tf,aux] = tfIfdl(s,locs,cellData)
```

  - Outputs are: frequency response `tf`, the high-frequency gains, the low-frequency (dc) gains, the integrator residue `res0`, and other auxiliary data that will become more important in Ch. 4.

- They are invoked by with a vector of complex frequencies s and a set of $\tilde{x}$ locations. Here is how to create a Bode plot:

```
clearvars; close all; clc;
cellData = loadCellParams('cellDoyle.xlsx');
omega = [0, logspace(-6,6,200)]; s = 1j*omega;
SOC = 0.8;              % Cell state of charge
T = 273.15 + 25;        % Temperature in K for 25 degC
cellData = evalSetpoint(cellData,s,SOC,T);

[Ifdl_tf,~] = tfIfdl(s,0:0.2:3,cellData);

subplot(2,1,1); semilogx(omega,20*log10(abs(Ifdl_tf)));
title('Magnitude response for i_{f+dl}');
ylabel('Magnitude (dB)'); xlabel('Frequency (rad/s)');
subplot(2,1,2); semilogx(omega,unwrap(angle(Ifdl_tf),[],2)*180/pi);
title('Phase response for Ifdl');
ylabel('Phase (deg)'); xlabel('Frequency (rad/s)');
```

- And, here is how to create a Nyquist plot of cell impedance:

```
clearvars; close all; clc;
cellData = loadCellParams('cellDoyleCPE.xlsx');
omega = [0, logspace(-6,6,200)]; s = 1j*omega;
SOC = 0.8;              % Cell state of charge
T = 273.15 + 25;        % Temperature in K for 25 degC
cellData = evalSetpoint(cellData,s,SOC,T);
```



```
[phise_tf,~] = tfPhiseInt(s,[0,3],cellData);
[phie_tf,~]  = tfPhie(s,3,cellData);
Z = -(phise_tf(2,:) - phise_tf(1,:) + phie_tf);

plot(real(1000*Z),-imag(1000*Z));
xlabel('Real'); h = ylabel('-Imag'); title('Impedance (milliohms)');
xlim([0 14]); ylim([0 14]); grid on; axis square;
```

- These two examples are included in the toolbox “CH2” folder.

Where to from here?

- Have now derived TFs of all cell electrochemical variables, and have seen how to combine several TFs to compute cell impedance.
- Implementing these TFs requires knowledge of parameter values.
- Next chapter will show how to use known PDEs and known structure of TFs along with cell-test data to estimate parameter values of physical cells using lab tests.

Appendix 2.a: Summary of new variables

- $\bar{C}_{\rm dl}$ [F], lumped double-layer capacitance. In terms of the standard-parameter definition, $\bar{C}_{\rm dl} = a_{\rm s}ALC_{\rm dl}$ where $C_{\rm dl}$ has units [F m^{-2}].
- $\bar{R}_{\rm dl}$ [Ω], lumped double-layer resistance. In terms of the standard-parameter definition, $\bar{R}_{\rm dl} = R_{\rm dl}/(a_{\rm s}AL)$ where $R_{\rm dl}$ has units [Ω m^2].
- $i_{\rm dl}$ [A], double-layer lithium flux. In terms of the standard-parameter definition, $i_{\rm dl} = a_{\rm s}ALj_{\rm dl}/F$ where $j_{\rm dl}$ has units [mol m^{-2} s^{-1}].
- $i_{\rm f}$ [A], lithium flux of lithium actually exiting particle. In terms of the standard-parameter definition, $i_{\rm f} = a_{\rm s}ALj_{\rm f}/F$ where $j_{\rm f}$ has units [mol m^{-2} s^{-1}].
- $\bar{Z}_{\rm s}(s)$ [Ω], ideal particle diffusion impedance

$$\bar{Z}_{\rm s}(s) = [U_{\rm ocp}]' \frac{|\theta_{100} - \theta_0|}{10\,800\bar{D}_{\rm s}Q} \left[\frac{1}{1 - \sqrt{s/\bar{D}_{\rm s}} \coth\left(\sqrt{s/\bar{D}_{\rm s}}\right)} \right].$$

- $\bar{Z}_{\tilde{\rm s}}(s)$ [Ω], particle diffusion impedance with CPE on $\bar{D}_{\rm s}$

$$\bar{Z}_{\tilde{\rm s}}(s) = [U_{\rm ocp}]' \frac{|\theta_{100} - \theta_0|}{10\,800\bar{D}_{\rm s}Q} \left[\frac{\beta_{\tilde{\rm s}}^2(s) + 3\left(1 - \beta_{\tilde{\rm s}}(s)\coth\left(\beta_{\tilde{\rm s}}(s)\right)\right)}{\beta_{\tilde{\rm s}}^2(s)\left(1 - \beta_{\tilde{\rm s}}(s)\coth\left(\beta_{\tilde{\rm s}}(s)\right)\right)} - \frac{3\bar{D}_{\rm s}}{s} \right]$$

$$\beta_{\tilde{\rm s}}(s) = \sqrt{s^{n_{\rm f}}/\bar{D}_{\rm s}}.$$

- $\bar{Z}_{\rm se}(s)$ [Ω], ideal overall solid–electrolyte interface impedance, including double layer and film resistance
- $\bar{Z}_{\tilde{\rm se}}(s) = \bar{Z}_{\tilde{\rm sf}}(s) + \bar{R}_{\rm f}$, overall solid–electrolyte interface impedance, including double layer and film resistance, with CPE on double layer (and possibly on $\bar{D}_{\rm s}$), where

$$\bar{Z}_{\tilde{\rm sf}}(s) = \left(\frac{1}{\bar{R}_{\rm ct} + \bar{Z}_{\tilde{\rm s}}(s)} + \frac{1}{\bar{Z}_{\tilde{\rm dl}}} \right)^{-1}$$

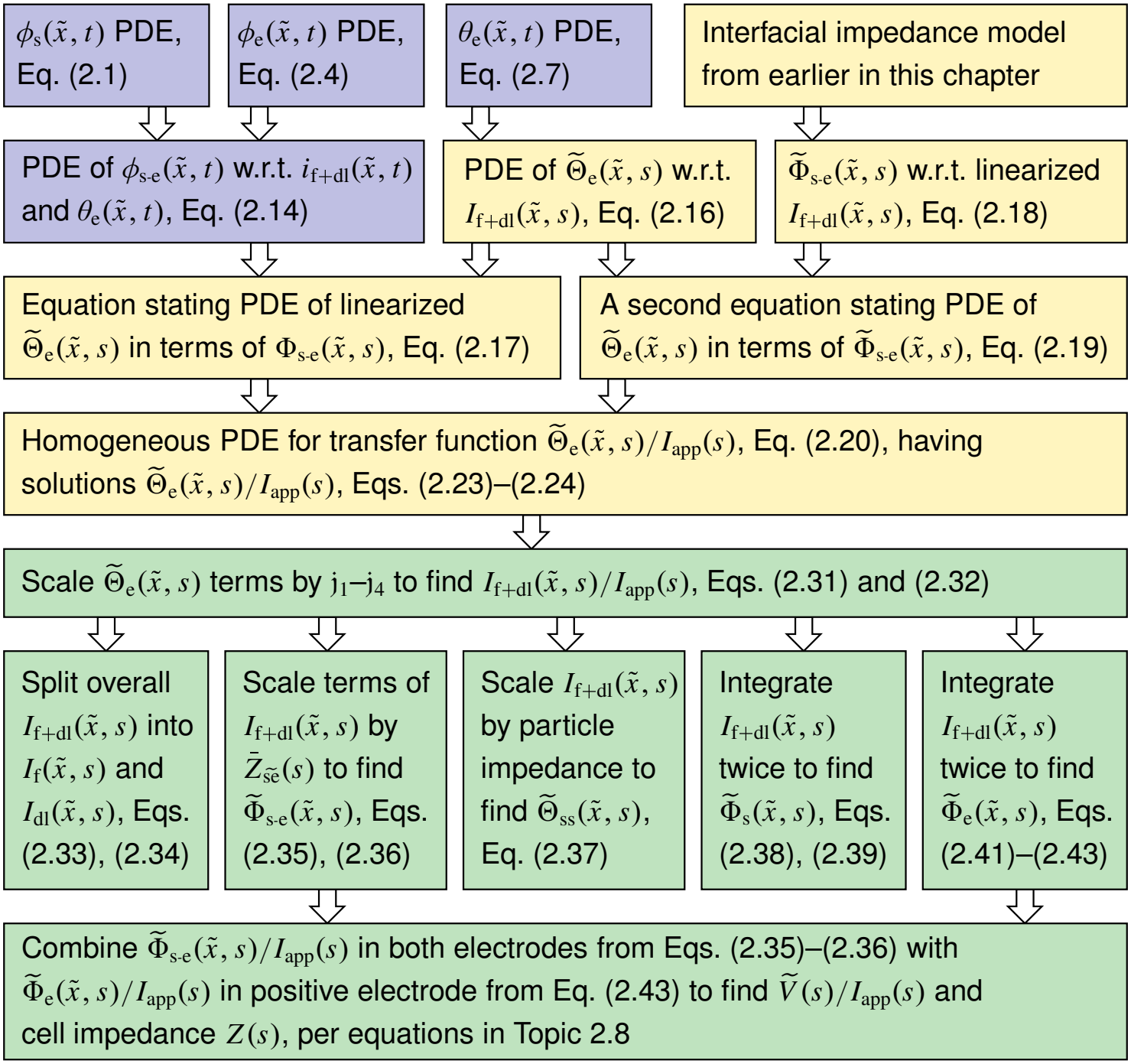
$$\bar{R}_{\rm ct} = RT/(\bar{i}_0 F)$$

$$\bar{i}_0 = \bar{k}_0(1 - \theta_{\rm s,0})^{1-\alpha}(\theta_{\rm s,0})^{\alpha}$$

$$\bar{Z}_{\tilde{\rm dl}} = \bar{R}_{\rm dl} + \frac{(s\bar{C}_{\rm dl} + \omega_{\rm dl})^{1-n_{\rm dl}}}{s\bar{C}_{\rm dl}^{2-n_{\rm dl}}}$$

Appendix 2.b: Deriving full-cell impedance model

- This appendix examines a method for deriving TFs without **A2**.
- The derivation is highly detailed. The flowchart below shows the process of the derivation, hoping to add clarity:



- Boxes shaded blue represent time domain; boxes shaded yellow represent frequency domain steps leading to $\widetilde{\Theta}_{\mathrm{e}}(\tilde{x}, s)/I_{\mathrm{app}}(s)$; boxes shaded in green represent TFs developed from $\widetilde{\Theta}_{\mathrm{e}}(\tilde{x}, s)/I_{\mathrm{app}}(s)$.
- First we find $\widetilde{\Theta}_{\mathrm{e}}(\tilde{x}, s)/I_{\mathrm{app}}(s)$; then, we find all other TFs based on it.
- For convenient reference, we repeat relevant PDEs here (remainder are summarized in Topic 2.6).
- PDE describing solid potential ϕ_{s} in cell region $\mathrm{r} \in \{\mathrm{n}, \mathrm{p}\}$ is

$$\bar{\sigma}^{\mathrm{r}} \frac{\partial^2 \phi_{\mathrm{s}}^{\mathrm{r}}(\tilde{x}, t)}{\partial \tilde{x}^2} = i_{\mathrm{f+dl}}^{\mathrm{r}}(\tilde{x}, t), \tag{2.1}$$

having boundary conditions

$$\bar{\sigma}^{\mathrm{r}} \left. \frac{\partial \phi_{\mathrm{s}}^{\mathrm{r}}(\tilde{x}, t)}{\partial \tilde{x}} \right|_{\tilde{x}=0,3} = -i_{\mathrm{app}}(t) \tag{2.2}$$

$$\bar{\sigma}^{\mathrm{r}} \left. \frac{\partial \phi_{\mathrm{s}}^{\mathrm{r}}(\tilde{x}, t)}{\partial \tilde{x}} \right|_{\tilde{x}=1,2} = 0. \tag{2.3}$$

- PDE describing electrolyte potential ϕ_{e} in cell region $\mathrm{r} \in \{\mathrm{n}, \mathrm{s}, \mathrm{p}\}$ (where $i_{\mathrm{f+dl}}^{\mathrm{s}}(\tilde{x}, t) = 0$) is

$$\frac{\partial}{\partial \tilde{x}} \left(\bar{\kappa}^{\mathrm{r}} \left(\frac{\partial \phi_{\mathrm{e}}^{\mathrm{r}}(\tilde{x}, t)}{\partial \tilde{x}} + \bar{\kappa}_D T \frac{\partial \ln \theta_{\mathrm{e}}^{\mathrm{r}}(\tilde{x}, t)}{\partial \tilde{x}} \right) \right) + i_{\mathrm{f+dl}}^{\mathrm{r}}(\tilde{x}, t) = 0 \tag{2.4}$$

having boundary conditions,

$$-\bar{\kappa}^{\mathrm{r}} \left[\left. \frac{\partial \phi_{\mathrm{e}}^{\mathrm{r}}(\tilde{x}, t)}{\partial \tilde{x}} + \bar{\kappa}_D T \frac{\partial \ln \theta_{\mathrm{e}}^{\mathrm{r}}(\tilde{x}, t)}{\partial \tilde{x}} \right|_{\tilde{x}=0,3} = 0 \tag{2.5}$$

$$-\bar{\kappa}^{\mathrm{r}} \left[\left. \frac{\partial \phi_{\mathrm{e}}^{\mathrm{r}}(\tilde{x}, t)}{\partial \tilde{x}} + \bar{\kappa}_D T \frac{\partial \ln \theta_{\mathrm{e}}^{\mathrm{r}}(\tilde{x}, t)}{\partial \tilde{x}} \right|_{\tilde{x}=1,2} = i_{\mathrm{app}}(t). \tag{2.6}$$

- PDE describing lithium concentration θ_{e} in electrolyte in cell region $\mathrm{r} \in \{\mathrm{n}, \mathrm{s}, \mathrm{p}\}$ is

$$3600\bar{q}_{\mathrm{e}}^{\mathrm{r}}\frac{\partial\theta_{\mathrm{e}}^{\mathrm{r}}(\tilde{x},t)}{\partial t}=\bar{\psi}^{\mathrm{r}}\frac{\partial}{\partial\tilde{x}}\bar{\kappa}^{\mathrm{r}}\frac{\partial}{\partial\tilde{x}}\theta_{\mathrm{e}}^{\mathrm{r}}(\tilde{x},t)+i_{\mathrm{f+dl}}^{\mathrm{r}}(\tilde{x},t) \tag{2.7}$$

having gradient boundary conditions,

$$\bar{\kappa}^{\mathrm{n}}\left.\frac{\partial\theta_{\mathrm{e}}^{\mathrm{n}}(\tilde{x},t)}{\partial\tilde{x}}\right|_{\tilde{x}=0}=0 \tag{2.8}$$

$$\bar{\kappa}^{\mathrm{n}}\left.\frac{\partial\theta_{\mathrm{e}}^{\mathrm{n}}(\tilde{x},t)}{\partial\tilde{x}}\right|_{\tilde{x}=1^{-}}=\bar{\kappa}^{\mathrm{s}}\left.\frac{\partial\theta_{\mathrm{e}}^{\mathrm{s}}(\tilde{x},t)}{\partial\tilde{x}}\right|_{\tilde{x}=1^{+}} \tag{2.9}$$

$$\bar{\kappa}^{\mathrm{s}}\left.\frac{\partial\theta_{\mathrm{e}}^{\mathrm{s}}(\tilde{x},t)}{\partial\tilde{x}}\right|_{\tilde{x}=2^{-}}=\bar{\kappa}^{\mathrm{p}}\left.\frac{\partial\theta_{\mathrm{e}}^{\mathrm{p}}(\tilde{x},t)}{\partial\tilde{x}}\right|_{\tilde{x}=2^{+}} \tag{2.10}$$

$$\bar{\kappa}^{\mathrm{p}}\left.\frac{\partial\theta_{\mathrm{e}}^{\mathrm{p}}(\tilde{x},t)}{\partial\tilde{x}}\right|_{\tilde{x}=3}=0 \tag{2.11}$$

and also continuity boundary conditions,

$$\theta_{\mathrm{e}}^{\mathrm{n}}(1^{-},t)=\theta_{\mathrm{e}}^{\mathrm{s}}(1^{+},t) \tag{2.12}$$

$$\theta_{\mathrm{e}}^{\mathrm{s}}(2^{-},t)=\theta_{\mathrm{e}}^{\mathrm{p}}(2^{+},t). \tag{2.13}$$

Finding form of transfer function $\widetilde{\Theta}_{\mathrm{e}}^{\mathrm{r}}(\tilde{x},s)/I_{\mathrm{app}}(s)$

- In this section, we find transfer function $\widetilde{\Theta}_{\mathrm{e}}^{\mathrm{r}}(\tilde{x},s)/I_{\mathrm{app}}(s)$, from which all other transfer functions are derived in later sections.
- For brevity, we omit superscripts $\mathrm{r}\in\{\mathrm{n},\mathrm{s},\mathrm{p}\}$ assuming a generic applicable region; when distinctions between regions become important, we will re-introduce superscript notation.
- We begin by subtracting Eq. (2.4) from Eq. (2.1),

$$\left[\frac{\partial^2\phi_{\mathrm{s}}(\tilde{x},t)}{\partial\tilde{x}^2}-\frac{1}{\bar{\sigma}}\,i_{\mathrm{f+dl}}(\tilde{x},t)=0\right]$$

$$-\left[\frac{\partial^2\phi_{\mathrm{e}}(\tilde{x},t)}{\partial\tilde{x}^2}+\bar{\kappa}_D T\frac{\partial^2\ln\theta_{\mathrm{e}}(\tilde{x},t)}{\partial\tilde{x}^2}+\frac{1}{\bar{\kappa}}\,i_{\mathrm{f+dl}}(\tilde{x},t)=0\right],$$

to find a PDE for electrode/electrolyte phase potential difference

$$\phi_{\text{s-e}}(\tilde{x},t) = \phi_{\text{s}}(\tilde{x},t) - \phi_{\text{e}}(\tilde{x},t)$$

$$\frac{\partial^2 \phi_{\text{s-e}}(\tilde{x},t)}{\partial \tilde{x}^2} = \left(\frac{1}{\bar{\sigma}} + \frac{1}{\bar{\kappa}}\right) i_{\text{f+dl}}(\tilde{x},t) + \bar{\kappa}_D T \frac{\partial^2 \ln \theta_{\text{e}}(\tilde{x},t)}{\partial \tilde{x}^2}. \tag{2.14}$$

- Linearize around $\theta_{\text{e}}(\tilde{x},t) \approx \theta_{\text{e},0} = 1$ and define $\tilde{\theta}_{\text{e}}(\tilde{x},t) = \theta_{\text{e}}(\tilde{x},t) - \theta_{\text{e},0}$; natural logarithm can be approximated using Taylor-series

$$\begin{aligned}\ln(\theta_{\text{e}}(\tilde{x},t)) &= \ln(\theta_{\text{e},0} + \tilde{\theta}_{\text{e}}(\tilde{x},t)) \\ &\approx \ln\theta_{\text{e},0} + \tilde{\theta}_{\text{e}}(\tilde{x},t)/\theta_{\text{e},0} = \tilde{\theta}_{\text{e}}(\tilde{x},t).\end{aligned}$$

- Then,

$$\frac{\partial^2 \phi_{\text{s-e}}(\tilde{x},t)}{\partial \tilde{x}^2} \approx \left(\frac{1}{\bar{\sigma}} + \frac{1}{\bar{\kappa}}\right) i_{\text{f+dl}}(\tilde{x},t) + \bar{\kappa}_D T \frac{\partial^2 \tilde{\theta}_{\text{e}}(\tilde{x},t)}{\partial \tilde{x}^2}$$

- We take the Laplace transform of this relationship,

$$\frac{\partial^2 \Phi_{\text{s-e}}(\tilde{x},s)}{\partial \tilde{x}^2} = \left(\frac{1}{\bar{\sigma}} + \frac{1}{\bar{\kappa}}\right) I_{\text{f+dl}}(\tilde{x},s) + \bar{\kappa}_D T \frac{\partial^2 \widetilde{\Theta}_{\text{e}}(\tilde{x},s)}{\partial \tilde{x}^2}. \tag{2.15}$$

- On the other hand, taking Laplace transform of Eq. (2.7),

$$I_{\text{f+dl}}(\tilde{x},s) = -\bar{\psi}\bar{\kappa}\frac{\partial^2 \widetilde{\Theta}_{\text{e}}(\tilde{x},s)}{\partial \tilde{x}^2} + 3600\bar{q}_{\text{e}} s \widetilde{\Theta}_{\text{e}}(\tilde{x},s). \tag{2.16}$$

- Substituting Eq. (2.16) into (2.15),

$$\begin{aligned}\frac{\partial^2 \Phi_{\text{s-e}}(\tilde{x},s)}{\partial \tilde{x}^2} = &\left(-\bar{\psi}\bar{\kappa}\left(\frac{1}{\bar{\sigma}} + \frac{1}{\bar{\kappa}}\right) + \bar{\kappa}_D T\right)\frac{\partial^2 \widetilde{\Theta}_{\text{e}}(\tilde{x},s)}{\partial \tilde{x}^2} \\ &+ 3600\bar{q}_{\text{e}}\left(\frac{1}{\bar{\sigma}} + \frac{1}{\bar{\kappa}}\right) s\widetilde{\Theta}_{\text{e}}(\tilde{x},s).\end{aligned} \tag{2.17}$$

- At this point, we have expressed the phase potential difference PDE as a function of only the electrolyte concentration.

- Notice that if we can somehow find another relationship between the phase potential difference and the electrolyte concentration, we will end up with an homogeneous PDE in $\widetilde{\Theta}_{\mathrm{e}}$ that can be solved.
- We start with the interfacial model found earlier in Topic 2.4:

$$\widetilde{\Phi}_{\text{s-e}}(s) = \bar{Z}_{\widetilde{\text{se}}}(s) I_{\text{f+dl}}(s).$$

- Note, this TF is the same at every spatial location, so can also write:

$$\widetilde{\Phi}_{\text{s-e}}(\tilde{x}, s) = \bar{Z}_{\widetilde{\text{se}}}(s) I_{\text{f+dl}}(\tilde{x}, s). \tag{2.18}$$

- From Eqs. (2.18) and (2.16), we can also find:

$$\widetilde{\Phi}_{\text{s-e}}(\tilde{x}, s) = \bar{Z}_{\widetilde{\text{se}}}(s) \left(-\bar{\psi}\bar{\kappa} \frac{\partial^2 \widetilde{\Theta}_{\mathrm{e}}(\tilde{x}, s)}{\partial \tilde{x}^2} + 3600 \bar{q}_{\mathrm{e}} s \widetilde{\Theta}_{\mathrm{e}}(\tilde{x}, s) \right). \tag{2.19}$$

- Recognizing $\partial^2 \Phi_{\text{s-e}}(\tilde{x}, s)/\partial \tilde{x}^2 = \partial^2 \widetilde{\Phi}_{\text{s-e}}(\tilde{x}, s)/\partial \tilde{x}^2$, rewrite Eq. (2.17):

$$-\bar{\psi}\bar{\kappa} \frac{\partial^4 \widetilde{\Theta}_{\mathrm{e}}(\tilde{x}, s)}{\partial \tilde{x}^4} + 3600 \bar{q}_{\mathrm{e}} s \frac{\partial^2 \widetilde{\Theta}_{\mathrm{e}}(\tilde{x}, s)}{\partial \tilde{x}^2} = \frac{3600 \bar{q}_{\mathrm{e}}}{\bar{Z}_{\widetilde{\text{se}}}(s)} \left(\frac{1}{\bar{\sigma}} + \frac{1}{\bar{\kappa}} \right) s \widetilde{\Theta}_{\mathrm{e}}(\tilde{x}, s)$$
$$+ \left(\frac{-\bar{\psi}\bar{\kappa}}{\bar{Z}_{\widetilde{\text{se}}}(s)} \left(\frac{1}{\bar{\sigma}} + \frac{1}{\bar{\kappa}} \right) + \frac{\bar{\kappa}_D T}{\bar{Z}_{\widetilde{\text{se}}}(s)} \right) \frac{\partial^2 \widetilde{\Theta}_{\mathrm{e}}(\tilde{x}, s)}{\partial \tilde{x}^2}.$$

- Rearranging, and dividing by $I_{\text{app}}(s)$ we get a fourth-order homogeneous PDE with unitless coefficients $\tau_1^{\mathrm{r}}(s)$ and $\tau_2^{\mathrm{r}}(s)$:

$$\frac{\partial^4}{\partial \tilde{x}^4} \frac{\widetilde{\Theta}_{\mathrm{e}}^{\mathrm{r}}(\tilde{x}, s)}{I_{\text{app}}(s)} - \tau_1^{\mathrm{r}}(s) \frac{\partial^2}{\partial \tilde{x}^2} \frac{\widetilde{\Theta}_{\mathrm{e}}^{\mathrm{r}}(\tilde{x}, s)}{I_{\text{app}}(s)} + \tau_2^{\mathrm{r}}(s) \frac{\widetilde{\Theta}_{\mathrm{e}}^{\mathrm{r}}(\tilde{x}, s)}{I_{\text{app}}(s)} = 0, \tag{2.20}$$

where,

$$\tau_1^{\mathrm{r}}(s) = \frac{3600 \bar{q}_{\mathrm{e}}^{\mathrm{r}} s}{\bar{\psi}\bar{\kappa}^{\mathrm{r}}} + \frac{1}{\bar{Z}_{\widetilde{\text{se}}}^{\mathrm{r}}(s)} \left(\frac{1}{\bar{\sigma}^{\mathrm{r}}} + \frac{1}{\bar{\kappa}^{\mathrm{r}}} \right) - \frac{\bar{\kappa}_D T}{\bar{\psi}\bar{\kappa}^{\mathrm{r}} \bar{Z}_{\widetilde{\text{se}}}^{\mathrm{r}}(s)}$$

$$\tau_2^{\mathrm{r}}(s) = \frac{3600 \bar{q}_{\mathrm{e}}^{\mathrm{r}} s}{\bar{\psi}\bar{\kappa}^{\mathrm{r}} \bar{Z}_{\widetilde{\text{se}}}^{\mathrm{r}}(s)} \left(\frac{1}{\bar{\sigma}^{\mathrm{r}}} + \frac{1}{\bar{\kappa}^{\mathrm{r}}} \right).$$

- The generic solution to the electrolyte concentration TF is then:[17]

$$\frac{\widetilde{\Theta}_{\mathrm{e}}^{\mathrm{r}}(\tilde{x},s)}{I_{\mathrm{app}}(s)} = \gamma_1^{\mathrm{r}}(s)e^{\Lambda_1^{\mathrm{r}}(s)\tilde{x}} + \gamma_2^{\mathrm{r}}(s)e^{-\Lambda_1^{\mathrm{r}}(s)\tilde{x}} + \gamma_3^{\mathrm{r}}(s)e^{\Lambda_2^{\mathrm{r}}(s)\tilde{x}} + \gamma_4^{\mathrm{r}}(s)e^{-\Lambda_2^{\mathrm{r}}(s)\tilde{x}} \tag{2.21}$$

  where,

$$\Lambda_1^{\mathrm{r}}(s) = \sqrt{\frac{1}{2}\left(\tau_1^{\mathrm{r}}(s) - \sqrt{(\tau_1^{\mathrm{r}}(s))^2 - 4\tau_2^{\mathrm{r}}(s)}\right)}$$

$$\Lambda_2^{\mathrm{r}}(s) = \sqrt{\frac{1}{2}\left(\tau_1^{\mathrm{r}}(s) + \sqrt{(\tau_1^{\mathrm{r}}(s))^2 - 4\tau_2^{\mathrm{r}}(s)}\right)}.$$

- Note that $\Lambda_1^{\mathrm{r}}(s)$ and $\Lambda_2^{\mathrm{r}}(s)$ have nonnegative real parts that tend toward infinity as $s \to \infty$, so, $\exp(\Lambda_1^{\mathrm{r}}(s))$ and $\exp(\Lambda_2^{\mathrm{r}}(s))$ have magnitudes that also approach infinity.
- For numeric robustness, we modify how we compute Eq. (2.21):
  - First, we define spatial variable $0 \le z \le 1$ (same as ECE5710) where:

$$z = \begin{cases} \tilde{x}, & \text{in the negative electrode} \\ \tilde{x} - 1, & \text{in the separator region} \\ 3 - \tilde{x}, & \text{in the positive electrode.} \end{cases}$$

[17] An alternate generic form of the solution is (where $\gamma_k^{\mathrm{r}}(s) \neq \bar{\gamma}_k^{\mathrm{r}}(s)$)

$$\frac{\widetilde{\Theta}_{\mathrm{e}}^{\mathrm{r}}(\tilde{x},s)}{I_{\mathrm{app}}(s)} = \bar{\gamma}_1^{\mathrm{r}}(s)\cosh(\Lambda_1^{\mathrm{r}}(s)\tilde{x}) + \bar{\gamma}_2^{\mathrm{r}}(s)\sinh(\Lambda_1^{\mathrm{r}}(s)\tilde{x}) + \bar{\gamma}_3^{\mathrm{r}}(s)\cosh(\Lambda_2^{\mathrm{r}}(s)\tilde{x}) + \bar{\gamma}_4^{\mathrm{r}}(s)\sinh(\Lambda_2^{\mathrm{r}}(s)\tilde{x}).$$

We have implemented both: while they are theoretically equivalent, I chose to present the exponential rather than the hyperbolic form since we find that its numeric performance at high frequencies is more robust in practice.

- Second, we rewrite Eq. (2.21) as:

$$\frac{\widetilde{\Theta}_{\mathrm{e}}^{\mathrm{r}}(z,s)}{I_{\mathrm{app}}(s)} = c_1^{\mathrm{r}}(s)e^{\Lambda_1^{\mathrm{r}}(s)(z-1)} + c_2^{\mathrm{r}}(s)e^{-\Lambda_1^{\mathrm{r}}(s)z} + c_3^{\mathrm{r}}(s)e^{\Lambda_2^{\mathrm{r}}(s)(z-1)} + c_4^{\mathrm{r}}(s)e^{-\Lambda_2^{\mathrm{r}}(s)z}. \tag{2.22}$$

- Notice that the input to $\exp(\cdot)$ now always has a nonpositive real part and so the $\exp(\cdot)$ function will produce a finite result.
- In this new formulation, $c_k^{\mathrm{r}}(s)$ are related to but different from $\gamma_k^{\mathrm{r}}(s)$. We will use this new formulation exclusively from this point forward.
- This solution corresponds to a generic electrode region. The specific electrolyte-concentration solutions for the two regions will be:
  - Negative-electrode region (where $z = \tilde{x}$):

$$\frac{\widetilde{\Theta}_{\mathrm{e}}^{\mathrm{n}}(z,s)}{I_{\mathrm{app}}(s)} = c_1^{\mathrm{n}}(s)e^{\Lambda_1^{\mathrm{n}}(s)(z-1)} + c_2^{\mathrm{n}}(s)e^{-\Lambda_1^{\mathrm{n}}(s)z} + c_3^{\mathrm{n}}(s)e^{\Lambda_2^{\mathrm{n}}(s)(z-1)} + c_4^{\mathrm{n}}(s)e^{-\Lambda_2^{\mathrm{n}}(s)z}. \tag{2.23}$$

  - Positive-electrode region (where $z = 3 - \tilde{x}$):

$$\frac{\widetilde{\Theta}_{\mathrm{e}}^{\mathrm{p}}(z,s)}{I_{\mathrm{app}}(s)} = c_1^{\mathrm{p}}(s)e^{\Lambda_1^{\mathrm{p}}(s)(z-1)} + c_2^{\mathrm{p}}(s)e^{-\Lambda_1^{\mathrm{p}}(s)z} + c_3^{\mathrm{p}}(s)e^{\Lambda_2^{\mathrm{p}}(s)(z-1)} + c_4^{\mathrm{p}}(s)e^{-\Lambda_2^{\mathrm{p}}(s)z}. \tag{2.24}$$

- In the separator, note that $i_{\mathrm{f+dl}}^{\mathrm{s}}(\tilde{x},t) = 0$ and $\phi_{\mathrm{s\text{-}e}}^{\mathrm{s}}(\tilde{x},t)$ does not exist.
- For this region then, directly from Eq. (2.7),

$$\frac{\partial^2}{\partial \tilde{x}^2}\frac{\widetilde{\Theta}_{\mathrm{e}}(\tilde{x},s)}{I_{\mathrm{app}}(s)} - \frac{3600\bar{q}_{\mathrm{e}}^{\mathrm{s}}s}{\bar{\psi}\bar{\kappa}^{\mathrm{s}}}\frac{\widetilde{\Theta}_{\mathrm{e}}(\tilde{x},s)}{I_{\mathrm{app}}(s)} = 0.$$

- The solution to this lower-order PDE is (where $z = \tilde{x} - 1$):

$$\frac{\widetilde{\Theta}_{\mathrm{e}}^{\mathrm{s}}(z,s)}{I_{\mathrm{app}}(s)} = c_1^{\mathrm{s}}(s)e^{\Lambda_1^{\mathrm{s}}(s)(z-1)} + c_2^{\mathrm{s}}(s)e^{-\Lambda_1^{\mathrm{s}}(s)z}, \tag{2.25}$$

where,

$$\Lambda_1^{\mathrm{s}}(s) = \sqrt{\frac{3600\bar{q}_{\mathrm{e}}^{\mathrm{s}}s}{\bar{\psi}\bar{\kappa}^{\mathrm{s}}}}, \quad \text{and there is no } \Lambda_2^{\mathrm{s}}(s).$$

- To summarize to this point: we have found a generic Laplace-domain relationship for $\widetilde{\Theta}_{\mathrm{e}}^{\mathrm{r}}(\tilde{x},s)/I_{\mathrm{app}}(s)$, written in terms of ten undetermined functions: $c_1^{\mathrm{n}}(s)$, $c_2^{\mathrm{n}}(s)$, $c_3^{\mathrm{n}}(s)$, $c_4^{\mathrm{n}}(s)$, $c_1^{\mathrm{s}}(s)$, $c_2^{\mathrm{s}}(s)$, $c_1^{\mathrm{p}}(s)$, $c_2^{\mathrm{p}}(s)$, $c_3^{\mathrm{p}}(s)$, $c_4^{\mathrm{p}}(s)$.
- Hence, to find $\widetilde{\Theta}_{\mathrm{e}}^{\mathrm{r}}(\tilde{x},s)/I_{\mathrm{app}}(s)$ at some point $\tilde{x}$ in the cell, we must first solve for these ten functions by using the ten boundary conditions of the ϕ_{s}, ϕ_{e}, and θ_{e} PDEs.

Solving for coefficients in $\widetilde{\Theta}_{\mathrm{e}}^{\mathrm{r}}(\tilde{x},s)/I_{\mathrm{app}}(s)$

- If the solid and electrolyte potential boundary conditions (BCs) stated in Eqs. (2.2), (2.3), (2.5), and (2.6) are combined,

$$\left.\frac{\partial\phi_{\text{s-e}}(\tilde{x},t)}{\partial\tilde{x}}\right|_{\tilde{x}=0,3} = -\frac{i_{\mathrm{app}}(t)}{\bar{\sigma}} + \bar{\kappa}_D T \underbrace{\left.\frac{\partial\tilde{\theta}_{\mathrm{e}}(\tilde{x},t)}{\partial\tilde{x}}\right|_{\tilde{x}=0,3}}_{0 \text{ by Eq. (2.8) or (2.11)}}$$

$$\left.\frac{\partial\phi_{\text{s-e}}(\tilde{x},t)}{\partial\tilde{x}}\right|_{\tilde{x}=1,2} = \frac{i_{\mathrm{app}}(t)}{\bar{\kappa}} + \bar{\kappa}_D T \left.\frac{\partial\tilde{\theta}_{\mathrm{e}}(\tilde{x},t)}{\partial\tilde{x}}\right|_{\tilde{x}=1,2}.$$

- Recognizing that $\partial\phi_{\text{s-e}}/\partial\tilde{x} = \partial\tilde{\phi}_{\text{s-e}}/\partial\tilde{x}$, Laplace transforms give:

$$\left.\frac{\partial\widetilde{\Phi}_{\text{s-e}}(\tilde{x},s)}{\partial\tilde{x}}\right|_{\tilde{x}=0,3} = -\frac{I_{\mathrm{app}}(s)}{\bar{\sigma}}$$

$$\left.\frac{\partial\widetilde{\Phi}_{\text{s-e}}(\tilde{x},s)}{\partial\tilde{x}}\right|_{\tilde{x}=1,2} = \frac{I_{\mathrm{app}}(s)}{\bar{\kappa}} + \bar{\kappa}_D T \left.\frac{\partial}{\partial\tilde{x}}\widetilde{\Theta}_{\mathrm{e}}(\tilde{x},s)\right|_{\tilde{x}=1,2}.$$

- To solve for the unknown coefficients, we must express all BCs in terms of the electrolyte-concentration.
- So, we reuse Eq. (2.19) and differentiate:

$$\widetilde{\Phi}_{\text{s-e}}(\tilde{x},s) = \bar{Z}_{\tilde{\text{se}}}(s)\left(-\bar{\psi}\bar{\kappa}\frac{\partial^2\widetilde{\Theta}_{\text{e}}(\tilde{x},s)}{\partial\tilde{x}^2} + 3600\bar{q}_{\text{e}}s\widetilde{\Theta}_{\text{e}}(\tilde{x},s)\right)$$

$$\frac{\partial\widetilde{\Phi}_{\text{s-e}}(\tilde{x},s)}{\partial\tilde{x}} = \bar{Z}_{\tilde{\text{se}}}(s)\left(-\bar{\psi}\bar{\kappa}\frac{\partial^3\widetilde{\Theta}_{\text{e}}(\tilde{x},s)}{\partial\tilde{x}^3} + 3600\bar{q}_{\text{e}}s\frac{\partial\widetilde{\Theta}_{\text{e}}(\tilde{x},s)}{\partial\tilde{x}}\right).$$

- At boundaries $\tilde{x} = 0, 3$, first-derivative term disappears and we have:

$$\left.\frac{\partial\widetilde{\Phi}_{\text{s-e}}(\tilde{x},s)}{\partial\tilde{x}}\right|_{\tilde{x}=0,3} = -\bar{\psi}\bar{\kappa}\bar{Z}_{\tilde{\text{se}}}(s)\frac{\partial^3\widetilde{\Theta}_{\text{e}}(\tilde{x},s)}{\partial\tilde{x}^3} = -\frac{I_{\text{app}}(s)}{\bar{\sigma}}$$

$$\left.\frac{\partial^3}{\partial\tilde{x}^3}\frac{\widetilde{\Theta}_{\text{e}}(\tilde{x},s)}{I_{\text{app}}(s)}\right|_{\tilde{x}=0,3} = \frac{1}{\bar{\sigma}\bar{\kappa}\bar{\psi}\bar{Z}_{\tilde{\text{se}}}(s)} = \frac{\mu_1(s)}{\bar{\sigma}}, \tag{2.26}$$

where we have defined:

$$\mu_1(s) = \frac{1}{\bar{\kappa}\bar{\psi}\bar{Z}_{\tilde{\text{se}}}(s)}.$$

- At boundaries $\tilde{x} = 1, 2$ we have:

$$\bar{Z}_{\tilde{\text{se}}}(s)\left(-\bar{\psi}\bar{\kappa}\frac{\partial^3\widetilde{\Theta}_{\text{e}}(\tilde{x},s)}{\partial\tilde{x}^3} + 3600\bar{q}_{\text{e}}s\frac{\partial\widetilde{\Theta}_{\text{e}}(\tilde{x},s)}{\partial\tilde{x}}\right) = \frac{I_{\text{app}}(s)}{\bar{\kappa}} + \bar{\kappa}_D T\frac{\partial}{\partial\tilde{x}}\widetilde{\Theta}_{\text{e}}(\tilde{x},s).$$

- Rearranging,

$$\left.\frac{\partial^3}{\partial\tilde{x}^3}\frac{\widetilde{\Theta}_{\text{e}}(\tilde{x},s)}{I_{\text{app}}(s)}\right|_{\tilde{x}=1,2} = -\frac{1}{\bar{\kappa}^2\bar{\psi}\bar{Z}_{\tilde{\text{se}}}(s)} - \frac{\bar{\kappa}_D T - 3600\bar{q}_{\text{e}}s\bar{Z}_{\tilde{\text{se}}}}{\bar{\psi}\bar{\kappa}\bar{Z}_{\tilde{\text{se}}}(s)}\frac{\partial}{\partial\tilde{x}}\frac{\widetilde{\Theta}_{\text{e}}(\tilde{x},s)}{I_{\text{app}}(s)}$$

$$= -\frac{\mu_1(s)}{\bar{\kappa}} - \mu_2(s)\left.\frac{\partial}{\partial\tilde{x}}\frac{\widetilde{\Theta}_{\text{e}}(\tilde{x},s)}{I_{\text{app}}(s)}\right|_{\tilde{x}=1,2}, \tag{2.27}$$

where we have defined:

$$\mu_2(s) = \frac{\bar{\kappa}_D T - 3600\bar{q}_{\text{e}}s\bar{Z}_{\tilde{\text{se}}}(s)}{\bar{\psi}\bar{\kappa}\bar{Z}_{\tilde{\text{se}}}(s)}.$$

- Since we know electrolyte-concentration equation form for electrode regions from Eq. (2.22), can compute partial derivatives:

$$\frac{\partial}{\partial z}\frac{\widetilde{\Theta}_{\rm e}(z,s)}{I_{\rm app}(s)} = c_1\Lambda_1 e^{\Lambda_1(z-1)} - c_2\Lambda_1 e^{-\Lambda_1 z} + c_3\Lambda_2 e^{\Lambda_2(z-1)} - c_4\Lambda_2 e^{-\Lambda_2 z} \tag{2.28}$$

$$\frac{\partial^3}{\partial z^3}\frac{\widetilde{\Theta}_{\rm e}(z,s)}{I_{\rm app}(s)} = c_1\Lambda_1^3 e^{\Lambda_1(z-1)} - c_2\Lambda_1^3 e^{-\Lambda_1 z} + c_3\Lambda_2^3 e^{\Lambda_2(z-1)} - c_4\Lambda_2^3 e^{-\Lambda_2 z}. \tag{2.29}$$

- Can also compute derivative from Eq. (2.25) for separator region:

$$\frac{\partial}{\partial z}\frac{\widetilde{\Theta}_{\rm e}(z,s)}{I_{\rm app}(s)} = c_1^{\rm s}\Lambda_1^{\rm s} e^{\Lambda_1^{\rm s}(z-1)} - c_2^{\rm s}\Lambda_1^{\rm s} e^{-\Lambda_1^{\rm s} z}. \tag{2.30}$$

- At $\tilde{x} = 0$ ($z^{\rm n} = 0$), we have two BC equations:
  - Combine Eqs. (2.8) and (2.28):

$$c_1^{\rm n}\Lambda_1^{\rm n} e^{-\Lambda_1^{\rm n}} - c_2^{\rm n}\Lambda_1^{\rm n} + c_3^{\rm n}\Lambda_2^{\rm n} e^{\Lambda_2^{\rm n}} - c_4^{\rm n}\Lambda_2^{\rm n} = 0.$$

  - Combine Eqs. (2.26) and (2.29):

$$c_1^{\rm n}(\Lambda_1^{\rm n})^3 e^{-\Lambda_1^{\rm n}} - c_2^{\rm n}(\Lambda_1^{\rm n})^3 + c_3^{\rm n}(\Lambda_2^{\rm n})^3 e^{-\Lambda_2^{\rm n}} - c_4^{\rm n}(\Lambda_2^{\rm n})^3 = \frac{\mu_1^{\rm n}}{\bar{\sigma}^{\rm n}}.$$

- At $\tilde{x} = 1$ ($z^{\rm n} = 1$ and $z^{\rm s} = 0$), we have three BC equations:
  - Combine Eqs. (2.9), (2.28), and (2.30):

$$\bar{\kappa}^{\rm n}\left(c_1^{\rm n}\Lambda_1^{\rm n} - c_2^{\rm n}\Lambda_1^{\rm n} e^{-\Lambda_1^{\rm n}} + c_3^{\rm n}\Lambda_2^{\rm n} - c_4^{\rm n}\Lambda_2^{\rm n} e^{-\Lambda_2^{\rm n}}\right) = \bar{\kappa}^{\rm s}\left(c_1^{\rm s}\Lambda_1^{\rm s} e^{-\Lambda_1^{\rm s}} - c_2^{\rm s}\Lambda_1^{\rm s}\right).$$

  - Combine Eqs. (2.12), (2.22), and (2.25):

$$c_1^{\rm n} + c_2^{\rm n} e^{-\Lambda_1^{\rm n}} + c_3^{\rm n} + c_4^{\rm n} e^{-\Lambda_2^{\rm n}} = c_1^{\rm s} e^{-\Lambda_1^{\rm s}} + c_2^{\rm s}.$$

  - Combine Eqs. (2.27), (2.28), and (2.29) at $\tilde{x} = 1^-$:

$$-\frac{\mu_1^{\rm n}}{\bar{\kappa}^{\rm n}} = c_1^{\rm n}\underbrace{\left[(\Lambda_1^{\rm n})^3+\mu_2^{\rm n}\Lambda_1^{\rm n}\right]}_{\lambda_1^{\rm n}} - c_2^{\rm n}\lambda_1^{\rm n}e^{-\Lambda_1^{\rm n}} + c_3^{\rm n}\underbrace{\left[(\Lambda_2^{\rm n})^3+\mu_2^{\rm n}\Lambda_2^{\rm n}\right]}_{\lambda_2^{\rm n}} - c_4^{\rm n}\lambda_2^{\rm n}e^{-\Lambda_2^{\rm n}},$$

where we define $\lambda_k^{\rm r} = (\Lambda_k^{\rm r})^3 + \mu_2^{\rm r}\Lambda_k^{\rm r}$.

- At $\tilde{x} = 2$ ($z^{\rm s} = 1$ and $z^{\rm p} = 1$), we have three BC equations (notice sign changes in positive-electrode derivatives because $\mathrm{d}z/\mathrm{d}\tilde{x} = -1$):
  - Combine Eqs. (2.10), (2.28), and (2.30):

$$\bar{\kappa}^{\rm s}\left(c_1^{\rm s}\Lambda_1^{\rm s} - c_2^{\rm s}\Lambda_1^{\rm s}e^{-\Lambda_1^{\rm s}}\right) = -\bar{\kappa}^{\rm p}\left(c_1^{\rm p}\Lambda_1^{\rm p} - c_2^{\rm p}\Lambda_1^{\rm p}e^{-\Lambda_1^{\rm p}} + c_3^{\rm p}\Lambda_2^{\rm p} - c_4^{\rm p}\Lambda_2^{\rm p}e^{-\Lambda_2^{\rm p}}\right).$$

  - Combine Eqs. (2.13), (2.22), and (2.25):

$$c_1^{\rm s} + c_2^{\rm s}e^{-\Lambda_1^{\rm s}} = c_1^{\rm p} + c_2^{\rm p}e^{-\Lambda_1^{\rm p}} + c_3^{\rm p} + c_4^{\rm p}e^{-\Lambda_2^{\rm p}}.$$

  - Combine Eqs. (2.27), (2.28), and (2.29) at $\tilde{x} = 2^+$:

$$\frac{\mu_1^{\rm p}}{\bar{\kappa}^{\rm p}} = c_1^{\rm p}\underbrace{\left[(\Lambda_1^{\rm p})^3+\mu_2^{\rm p}\Lambda_1^{\rm p}\right]}_{\lambda_1^{\rm p}} - c_2^{\rm p}\lambda_1^{\rm p}e^{-\Lambda_1^{\rm p}} + c_3^{\rm p}\underbrace{\left[(\Lambda_2^{\rm p})^3+\mu_2^{\rm p}\Lambda_2^{\rm p}\right]}_{\lambda_2^{\rm p}} - c_4^{\rm p}\lambda_2^{\rm p}e^{-\Lambda_2^{\rm p}}.$$

- At $\tilde{x} = 3$ ($z^{\rm p} = 0$), we have two BC equations (notice sign changes in positive-electrode derivatives because $\mathrm{d}z/\mathrm{d}\tilde{x} = -1$):
  - Combine Eqs. (2.11) and (2.28)

$$c_1^{\rm p}\Lambda_1^{\rm p}e^{-\Lambda_1^{\rm p}} - c_2^{\rm p}\Lambda_1^{\rm p} + c_3^{\rm p}\Lambda_2^{\rm p}e^{-\Lambda_2^{\rm p}} - c_4^{\rm p}\Lambda_2^{\rm p} = 0.$$

  - Combine Eqs. (2.26) and (2.29)

$$c_1^{\rm p}(\Lambda_1^{\rm p})^3e^{-\Lambda_1^{\rm p}} - c_2^{\rm p}(\Lambda_1^{\rm p})^3 + c_3^{\rm p}(\Lambda_2^{\rm p})^3e^{-\Lambda_2^{\rm p}} - c_4^{\rm p}(\Lambda_2^{\rm p})^3 = -\frac{\mu_1^{\rm p}}{\bar{\sigma}^{\rm p}}.$$

- All of these BCs may be assembled in matrix form $\mathbf{Ac} = \mathbf{b}$ (see below).
  - As long as $\mathbf{A}$ is nonsingular and well-conditioned, can determine constants numerically as $\mathbf{c} = \mathbf{A}^{-1}\mathbf{b}$ at every frequency of interest.

$$
\begin{bmatrix}
\Lambda_1^{\mathrm{n}} e^{-\Lambda_1^{\mathrm{n}}} & -\Lambda_1^{\mathrm{n}} & \Lambda_2^{\mathrm{n}} e^{-\Lambda_2^{\mathrm{n}}} & -\Lambda_2^{\mathrm{n}} & 0 & 0 \\
(\Lambda_1^{\mathrm{n}})^3 e^{-\Lambda_1^{\mathrm{n}}} & -(\Lambda_1^{\mathrm{n}})^3 & (\Lambda_2^{\mathrm{n}})^3 e^{-\Lambda_2^{\mathrm{n}}} & -(\Lambda_2^{\mathrm{n}})^3 & 0 & 0 \\
\bar{\kappa}^{\mathrm{n}} \Lambda_1^{\mathrm{n}} & -\bar{\kappa}^{\mathrm{n}} \Lambda_1^{\mathrm{n}} e^{-\Lambda_1^{\mathrm{n}}} & \bar{\kappa}^{\mathrm{n}} \Lambda_2^{\mathrm{n}} & -\bar{\kappa}^{\mathrm{n}} \Lambda_2^{\mathrm{n}} e^{-\Lambda_2^{\mathrm{n}}} & -\bar{\kappa}^{\mathrm{s}} \Lambda_1^{\mathrm{s}} e^{-\Lambda_1^{\mathrm{s}}} & \bar{\kappa}^{\mathrm{s}} \Lambda_1^{\mathrm{s}} \\
1 & e^{-\Lambda_1^{\mathrm{n}}} & 1 & e^{-\Lambda_2^{\mathrm{n}}} & -e^{-\Lambda_1^{\mathrm{s}}} & -1 \\
\lambda_1^{\mathrm{n}} & -\lambda_1^{\mathrm{n}} e^{-\Lambda_1^{\mathrm{n}}} & \lambda_2^{\mathrm{n}} & -\lambda_2^{\mathrm{n}} e^{-\Lambda_2^{\mathrm{n}}} & 0 & 0 \\
0 & 0 & 0 & 0 & \bar{\kappa}^{\mathrm{s}} \Lambda_1^{\mathrm{s}} & -\bar{\kappa}^{\mathrm{s}} \Lambda_1^{\mathrm{s}} e^{-\Lambda_1^{\mathrm{s}}} \\
0 & 0 & 0 & 0 & 1 & e^{-\Lambda_1^{\mathrm{s}}} \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0
\end{bmatrix} \cdots
$$

$$
\begin{bmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
\bar{\kappa}^{\mathrm{p}} \Lambda_1^{\mathrm{p}} & -\bar{\kappa}^{\mathrm{p}} \Lambda_1^{\mathrm{p}} e^{-\Lambda_1^{\mathrm{p}}} & \bar{\kappa}^{\mathrm{p}} \Lambda_2^{\mathrm{p}} & -\bar{\kappa}^{\mathrm{p}} \Lambda_2^{\mathrm{p}} e^{-\Lambda_2^{\mathrm{p}}} \\
-1 & -e^{-\Lambda_1^{\mathrm{p}}} & -1 & -e^{-\Lambda_2^{\mathrm{p}}} \\
\lambda_1^{\mathrm{p}} & -\lambda_1^{\mathrm{p}} e^{-\Lambda_1^{\mathrm{p}}} & \lambda_2^{\mathrm{p}} & -\lambda_2^{\mathrm{p}} e^{-\Lambda_2^{\mathrm{p}}} \\
\Lambda_1^{\mathrm{p}} e^{-\Lambda_1^{\mathrm{p}}} & -\Lambda_1^{\mathrm{p}} & \Lambda_2^{\mathrm{p}} e^{-\Lambda_2^{\mathrm{p}}} & -\Lambda_2^{\mathrm{p}} \\
(\Lambda_1^{\mathrm{p}})^3 e^{-\Lambda_1^{\mathrm{p}}} & -(\Lambda_1^{\mathrm{p}})^3 & (\Lambda_2^{\mathrm{p}})^3 e^{-\Lambda_2^{\mathrm{p}}} & -(\Lambda_2^{\mathrm{p}})^3
\end{bmatrix}
\begin{bmatrix}
c_1^{\mathrm{n}} \\ c_2^{\mathrm{n}} \\ c_3^{\mathrm{n}} \\ c_4^{\mathrm{n}} \\ c_1^{\mathrm{s}} \\ c_2^{\mathrm{s}} \\ c_1^{\mathrm{p}} \\ c_2^{\mathrm{p}} \\ c_3^{\mathrm{p}} \\ c_4^{\mathrm{p}}
\end{bmatrix}
=
\begin{bmatrix}
0 \\ \mu_1^{\mathrm{n}}/\bar{\sigma}^{\mathrm{n}} \\ 0 \\ 0 \\ -\mu_1^{\mathrm{n}}/\bar{\kappa}^{\mathrm{n}} \\ 0 \\ 0 \\ \mu_1^{\mathrm{p}}/\bar{\kappa}^{\mathrm{p}} \\ 0 \\ -\mu_1^{\mathrm{p}}/\bar{\sigma}^{\mathrm{p}}
\end{bmatrix}.
$$

- Alternately, we can solve these ten equations for a closed-form solution: this solution is given in App. 2.c.

Interfacial lithium-flux transfer function

- Derivation of $\widetilde{\Theta}_{\mathrm{e}}(\tilde{x}, s)/I_{\mathrm{app}}(s)$ unlocks remaining electrochemical-variable TFs as they can all be written in terms of $\widetilde{\Theta}_{\mathrm{e}}(\tilde{x}, s)$.

- We begin by looking at the interfacial lithium flux.
- Recall that the interfacial lithium flux is expressed as a function of the electrolyte concentration in Eq. (2.16):

$$I_{\text{f+dl}}(\tilde{x},s) = -\bar{\psi}\bar{\kappa}\frac{\partial^2\widetilde{\Theta}_{\text{e}}(\tilde{x},s)}{\partial\tilde{x}^2} + 3600\bar{q}_{\text{e}}s\,\widetilde{\Theta}_{\text{e}}(\tilde{x},s).$$

- In the negative electrode, we can write ($z = \tilde{x} = 0\ldots 1$):

$$\begin{aligned}\frac{I^{\text{n}}_{\text{f+dl}}(z,s)}{I_{\text{app}}(s)} &= -\bar{\psi}\bar{\kappa}^{\text{n}}\Big(c^{\text{n}}_1\left(\Lambda^{\text{n}}_1\right)^2 e^{\Lambda^{\text{n}}_1(z-1)} + c^{\text{n}}_2\left(\Lambda^{\text{n}}_1\right)^2 e^{-\Lambda^{\text{n}}_1 z} \\ &\quad + c^{\text{n}}_3\left(\Lambda^{\text{n}}_2\right)^2 e^{\Lambda^{\text{n}}_2(z-1)} + c^{\text{n}}_4\left(\Lambda^{\text{n}}_2\right)^2 e^{-\Lambda^{\text{n}}_2 z}\Big) \\ &\quad + 3600\bar{q}^{\text{n}}_{\text{e}}s\left(c^{\text{n}}_1 e^{\Lambda^{\text{n}}_1(z-1)} + c^{\text{n}}_2 e^{-\Lambda^{\text{n}}_1 z} + c^{\text{n}}_3 e^{\Lambda^{\text{n}}_2(z-1)} + c^{\text{n}}_4 e^{-\Lambda^{\text{n}}_2 z}\right) \\ &= \mathrm{j}^{\text{n}}_1 e^{\Lambda^{\text{n}}_1(z-1)} + \mathrm{j}^{\text{n}}_2 e^{-\Lambda^{\text{n}}_1 z} + \mathrm{j}^{\text{n}}_3 e^{\Lambda^{\text{n}}_2(z-1)} + \mathrm{j}^{\text{n}}_4 e^{-\Lambda^{\text{n}}_2 z}, \end{aligned} \tag{2.31}$$

  where the equation subfunctions j^{n}_1 through j^{n}_4 are given by:

$$\mathrm{j}^{\text{n}}_1 = c^{\text{n}}_1\left(-\bar{\psi}\bar{\kappa}^{\text{n}}\left(\Lambda^{\text{n}}_1\right)^2 + 3600\bar{q}^{\text{n}}_{\text{e}}s\right), \quad \mathrm{j}^{\text{n}}_2 = c^{\text{n}}_2\left(-\bar{\psi}\bar{\kappa}^{\text{n}}\left(\Lambda^{\text{n}}_1\right)^2 + 3600\bar{q}^{\text{n}}_{\text{e}}s\right),$$

$$\mathrm{j}^{\text{n}}_3 = c^{\text{n}}_3\left(-\bar{\psi}\bar{\kappa}^{\text{n}}\left(\Lambda^{\text{n}}_2\right)^2 + 3600\bar{q}^{\text{n}}_{\text{e}}s\right), \quad \mathrm{j}^{\text{n}}_4 = c^{\text{n}}_4\left(-\bar{\psi}\bar{\kappa}^{\text{n}}\left(\Lambda^{\text{n}}_2\right)^2 + 3600\bar{q}^{\text{n}}_{\text{e}}s\right).$$

- There is no reaction in the separator region because of the absence of solid material: $I^{\text{s}}_{\text{f+dl}}(z,s) = 0$.
- In the positive electrode, we can write ($z = 3 - \tilde{x}$):

$$\frac{I^{\text{p}}_{\text{f+dl}}(z,s)}{I_{\text{app}}(s)} = \mathrm{j}^{\text{p}}_1 e^{\Lambda^{\text{p}}_1(z-1)} + \mathrm{j}^{\text{p}}_2 e^{-\Lambda^{\text{p}}_1 z} + \mathrm{j}^{\text{p}}_3 e^{\Lambda^{\text{p}}_2(z-1)} + \mathrm{j}^{\text{p}}_4 e^{-\Lambda^{\text{p}}_2 z}, \tag{2.32}$$

  where the equation subfunctions j^{p}_1 through j^{p}_4 are given by:

$$\mathrm{j}^{\text{p}}_1 = c^{\text{p}}_1\left(-\bar{\psi}\bar{\kappa}^{\text{p}}\left(\Lambda^{\text{p}}_1\right)^2 + 3600\bar{q}^{\text{p}}_{\text{e}}s\right), \quad \mathrm{j}^{\text{p}}_2 = c^{\text{p}}_2\left(-\bar{\psi}\bar{\kappa}^{\text{p}}\left(\Lambda^{\text{p}}_1\right)^2 + 3600\bar{q}^{\text{p}}_{\text{e}}s\right),$$

$$\mathrm{j}^{\text{p}}_3 = c^{\text{p}}_3\left(-\bar{\psi}\bar{\kappa}^{\text{p}}\left(\Lambda^{\text{p}}_2\right)^2 + 3600\bar{q}^{\text{p}}_{\text{e}}s\right), \quad \mathrm{j}^{\text{p}}_4 = c^{\text{p}}_4\left(-\bar{\psi}\bar{\kappa}^{\text{p}}\left(\Lambda^{\text{p}}_2\right)^2 + 3600\bar{q}^{\text{p}}_{\text{e}}s\right).$$

Faradaic interfacial lithium-flux transfer function

- We will need to know the faradaic lithium flux $i_{\mathrm{f}}^{\mathrm{r}}$ to compute overpotential and cell voltage; however, its calculation depends on the exact interfacial model used.
- For the default simplified model of Topic 2.6, we can write:

$$I_{\mathrm{f}}(\tilde{x},s) = \frac{\bar{Z}_{\widetilde{\mathrm{dl}}}(s)}{\bar{R}_{\mathrm{ct}} + \bar{Z}_{\tilde{\mathrm{s}}}(s) + \bar{Z}_{\widetilde{\mathrm{dl}}}(s)} I_{\mathrm{f+dl}}(\tilde{x},s)$$

$$\bar{Z}_{\widetilde{\mathrm{dl}}}(s) = \bar{R}_{\mathrm{dl}} + \frac{(s\bar{C}_{\mathrm{dl}} + \omega_{\mathrm{dl}})^{(1-n_{\mathrm{dl}})}}{s(\bar{C}_{\mathrm{dl}})^{2-n_{\mathrm{dl}}}}.$$

- Therefore,

$$\frac{I_{\mathrm{f}}^{\mathrm{r}}(\tilde{x},s)}{I_{\mathrm{app}}(s)} = \frac{\bar{Z}_{\widetilde{\mathrm{dl}}}^{\mathrm{r}}(s)}{\bar{R}_{\mathrm{ct}}^{\mathrm{r}} + \bar{Z}_{\mathrm{Q}}^{\mathrm{r}}(s) + \bar{Z}_{\widetilde{\mathrm{dl}}}^{\mathrm{r}}(s)} \frac{I_{\mathrm{f+dl}}^{\mathrm{r}}(\tilde{x},s)}{I_{\mathrm{app}}(s)}. \tag{2.33}$$

- Once $I_{\mathrm{f+dl}}^{\mathrm{r}}(\tilde{x},s)/I_{\mathrm{app}}(s)$ is computed, it is then a simple matter to compute $I_{\mathrm{f}}^{\mathrm{r}}(\tilde{x},s)/I_{\mathrm{app}}(s)$.

Nonfaradaic interfacial lithium-flux transfer function

- By similar arguments,

$$\frac{I_{\mathrm{dl}}^{\mathrm{r}}(\tilde{x},s)}{I_{\mathrm{app}}(s)} = \frac{\bar{R}_{\mathrm{ct}}^{\mathrm{r}} + \bar{Z}_{\mathrm{Q}}^{\mathrm{r}}(s)}{\bar{R}_{\mathrm{ct}}^{\mathrm{r}} + \bar{Z}_{\mathrm{Q}}^{\mathrm{r}}(s) + \bar{Z}_{\widetilde{\mathrm{dl}}}^{\mathrm{r}}(s)} \frac{I_{\mathrm{f+dl}}^{\mathrm{r}}(\tilde{x},s)}{I_{\mathrm{app}}(s)}. \tag{2.34}$$

Phase-potential-difference transfer function

- The phase-potential-difference transfer function can be found by using Eq. (2.18), repeated here for convenience:

$$\widetilde{\Phi}_{\text{s-e}}(\tilde{x},s) = \bar{Z}_{\widetilde{\mathrm{se}}}(s) I_{\mathrm{f+dl}}^{\mathrm{r}}(\tilde{x},s).$$

- The negative-electrode transfer function can be written ($z = \tilde{x}$):

$$\frac{\widetilde{\Phi}^{\mathrm{n}}_{\mathrm{s\text{-}e}}(z,s)}{I_{\mathrm{app}}(s)} = \bar{Z}^{\mathrm{n}}_{\widetilde{\mathrm{se}}}(s)\frac{I^{\mathrm{r}}_{\mathrm{f+dl}}(z,s)}{I_{\mathrm{app}}(s)}$$
$$= \bar{Z}^{\mathrm{n}}_{\widetilde{\mathrm{se}}}(s)\left(\mathrm{j}^{\mathrm{n}}_1 e^{\Lambda^{\mathrm{n}}_1(z-1)} + \mathrm{j}^{\mathrm{n}}_2 e^{-\Lambda^{\mathrm{n}}_1 z} + \mathrm{j}^{\mathrm{n}}_3 e^{\Lambda^{\mathrm{n}}_2(z-1)} + \mathrm{j}^{\mathrm{n}}_4 e^{-\Lambda^{\mathrm{n}}_2 z}\right). \quad (2.35)$$

- There is no phase potential difference in the separator since $\widetilde{\Phi}_{\mathrm{s}}$ is undefined in that region.

- Similarly, the positive-electrode transfer function can be written:

$$\frac{\widetilde{\Phi}^{\mathrm{p}}_{\mathrm{s\text{-}e}}(z,s)}{I_{\mathrm{app}}(s)} = \bar{Z}^{\mathrm{p}}_{\widetilde{\mathrm{se}}}(s)\left(\mathrm{j}^{\mathrm{p}}_1 e^{\Lambda^{\mathrm{p}}_1(z-1)} + \mathrm{j}^{\mathrm{p}}_2 e^{-\Lambda^{\mathrm{p}}_1 z} + \mathrm{j}^{\mathrm{p}}_3 e^{\Lambda^{\mathrm{p}}_2(z-1)} + \mathrm{j}^{\mathrm{p}}_4 e^{-\Lambda^{\mathrm{p}}_2 z}\right), \quad (2.36)$$

  where $z = 3 - \tilde{x}$.

Solid-surface-concentration transfer function

- We determine solid-surface-concentration TF in stepwise fashion:

$$\frac{\widetilde{\Theta}_{\mathrm{ss}}(\tilde{x},s)}{I_{\mathrm{app}}(s)} = \frac{\widetilde{\Theta}_{\mathrm{ss}}(\tilde{x},s)}{I_{\mathrm{f}}(\tilde{x},s)}\frac{I_{\mathrm{f}}(\tilde{x},s)}{I_{\mathrm{app}}(s)}.$$

- First term depends on particle impedance and the OCP function:

$$\frac{\widetilde{\Theta}_{\mathrm{ss}}(\tilde{x},s)}{I_{\mathrm{f}}(\tilde{x},s)} = \frac{\bar{Z}_{\tilde{\mathrm{s}}}(s)}{[U_{\mathrm{ocp}}]'}.$$

- Then, we can write for $\mathrm{r} \in \{\mathrm{n}, \mathrm{p}\}$:

$$\frac{\widetilde{\Theta}^{\mathrm{r}}_{\mathrm{ss}}(\tilde{x},s)}{I_{\mathrm{app}}(s)} = \frac{\bar{Z}^{\mathrm{r}}_{\tilde{\mathrm{s}}}(s)}{[U^{\mathrm{r}}_{\mathrm{ocp}}]'}\frac{\bar{Z}^{\mathrm{r}}_{\widetilde{\mathrm{dl}}}(s)}{\bar{R}^{\mathrm{r}}_{\mathrm{ct}} + \bar{Z}^{\mathrm{r}}_{\tilde{\mathrm{s}}}(s) + \bar{Z}^{\mathrm{r}}_{\widetilde{\mathrm{dl}}}(s)}\frac{I^{\mathrm{r}}_{\mathrm{f+dl}}(\tilde{x},s)}{I_{\mathrm{app}}(s)}. \quad (2.37)$$

- This can be specialized for the positive and negative-electrode regions by appropriate substitutions of constants.

Solid-potential transfer function

- To find a transfer function for the solid potential, we must integrate Eq. (2.1) twice with respect to $\tilde{x}$.
- First, the electronic current that flows through the solid at any location $\tilde{x}$ is defined as $i_{\mathrm{s}}(\tilde{x}, t)$.
- The PDE governing $i_{\mathrm{s}}(\tilde{x}, t)$ is (temporarily using some non-lumped standard parameters):

$$-\varepsilon_{\mathrm{s}} A \frac{\partial}{\partial \tilde{x}} i_{\mathrm{s}}(\tilde{x}, t) = i_{\mathrm{f+dl}}(\tilde{x}, t),$$

  which has limiting cases $\varepsilon_{\mathrm{s}} A i_{\mathrm{s}}(0, t) = i_{\mathrm{app}}(t)$ and $\varepsilon_{\mathrm{s}} A i_{\mathrm{s}}(1, t) = 0$.
  - Note that we do not know either ε_{s} or A, but these quantities will disappear in the derivation.
- Integrating both sides of the equation:

$$-\varepsilon_{\mathrm{s}} A \int_0^{\tilde{x}} \frac{\partial I_{\mathrm{s}}^{\mathrm{n}}(\xi, s)}{\partial \xi} \, \mathrm{d}\xi = \int_0^{\tilde{x}} I_{\mathrm{f+dl}}^{\mathrm{n}}(\xi, s) \, \mathrm{d}\xi$$

$$-\varepsilon_{\mathrm{s}} A \left[I_{\mathrm{s}}^{\mathrm{n}}(\tilde{x}, s) - I_{\mathrm{s}}^{\mathrm{n}}(0, s) \right] = \int_0^{\tilde{x}} I_{\mathrm{f+dl}}^{\mathrm{n}}(\xi, s) \, \mathrm{d}\xi$$

$$-\varepsilon_{\mathrm{s}} A I_{\mathrm{s}}^{\mathrm{n}}(\tilde{x}, s) + I_{\mathrm{app}}(s) = \int_0^{\tilde{x}} I_{\mathrm{f+dl}}^{\mathrm{n}}(\xi, s) \, \mathrm{d}\xi$$

$$\varepsilon_{\mathrm{s}} A \frac{I_{\mathrm{s}}^{\mathrm{n}}(\tilde{x}, s)}{I_{\mathrm{app}}(s)} = 1 - \int_0^{\tilde{x}} \frac{I_{\mathrm{f+dl}}^{\mathrm{n}}(\xi, s)}{I_{\mathrm{app}}(s)} \, \mathrm{d}\xi$$

- The transfer function for $I_{\mathrm{s}}(z, s)$ with respect to the input current for the negative electrode can then be found (substituting $z = \tilde{x}$, $\zeta = \xi$):

$$\varepsilon_{\mathrm{s}}^{\mathrm{n}} A \frac{I_{\mathrm{s}}^{\mathrm{n}}(z, s)}{I_{\mathrm{app}}(s)} = 1 - \int_0^{z} \frac{I_{\mathrm{f+dl}}^{\mathrm{n}}(\zeta, s)}{I_{\mathrm{app}}(s)} \, \mathrm{d}\zeta$$

$$= 1 - \int_0^z \mathrm{j}_1^{\mathrm{n}} e^{\Lambda_1^{\mathrm{n}}(\zeta-1)} + \mathrm{j}_2^{\mathrm{n}} e^{-\Lambda_1^{\mathrm{n}}\zeta} + \mathrm{j}_3^{\mathrm{n}} e^{\Lambda_2^{\mathrm{n}}(\zeta-1)} + \mathrm{j}_4^{\mathrm{n}} e^{-\Lambda_2^{\mathrm{n}}\zeta}\,\mathrm{d}\zeta$$

$$= 1 - \mathrm{j}_1^{\mathrm{n}} e^{-\Lambda_1^{\mathrm{n}}} \frac{e^{\Lambda_1^{\mathrm{n}} z} - 1}{\Lambda_1^{\mathrm{n}}} + \mathrm{j}_2^{\mathrm{n}} \frac{e^{-\Lambda_1^{\mathrm{n}} z} - 1}{\Lambda_1^{\mathrm{n}}} - \mathrm{j}_3^{\mathrm{n}} e^{-\Lambda_2^{\mathrm{n}}} \frac{e^{\Lambda_2^{\mathrm{n}} z} - 1}{\Lambda_2^{\mathrm{n}}} + \mathrm{j}_4^{\mathrm{n}} \frac{e^{-\Lambda_2^{\mathrm{n}} z} - 1}{\Lambda_2^{\mathrm{n}}}.$$

- Can now solve for solid potential by defining $\tilde{\phi}_{\mathrm{s}}(\tilde{x}, t) = \phi_{\mathrm{s}}(\tilde{x}, t) - \phi_{\mathrm{s}}(0, t)$ and integrating again, giving:

$$\frac{\widetilde{\Phi}_{\mathrm{s}}^{\mathrm{n}}(z, s)}{I_{\mathrm{app}}(s)} = -\frac{1}{\bar{\sigma}^{\mathrm{n}}} \int_0^z \varepsilon_{\mathrm{s}}^{\mathrm{n}} A \frac{I_{\mathrm{s}}^{\mathrm{n}}(\zeta, s)}{I_{\mathrm{app}}(s)}\,\mathrm{d}\zeta$$

$$= -\frac{z}{\bar{\sigma}^{\mathrm{n}}} + \frac{\mathrm{j}_1^{\mathrm{n}} \left(e^{\Lambda_1^{\mathrm{n}}(z-1)} - e^{-\Lambda_1^{\mathrm{n}}} - z\Lambda_1^{\mathrm{n}} e^{-\Lambda_1^{\mathrm{n}}} \right)}{\bar{\sigma}^{\mathrm{n}} \left(\Lambda_1^{\mathrm{n}} \right)^2} + \frac{\mathrm{j}_2^{\mathrm{n}} \left(e^{-\Lambda_1^{\mathrm{n}} z} - 1 + z\Lambda_1^{\mathrm{n}} \right)}{\bar{\sigma}^{\mathrm{n}} \left(\Lambda_1^{\mathrm{n}} \right)^2}$$

$$+ \frac{\mathrm{j}_3^{\mathrm{n}} \left(e^{\Lambda_2^{\mathrm{n}}(z-1)} - e^{-\Lambda_2^{\mathrm{n}}} - z\Lambda_2^{\mathrm{n}} e^{-\Lambda_2^{\mathrm{n}}} \right)}{\bar{\sigma}^{\mathrm{n}} \left(\Lambda_2^{\mathrm{n}} \right)^2} + \frac{\mathrm{j}_4^{\mathrm{n}} \left(e^{-\Lambda_2^{\mathrm{n}} z} - 1 + z\Lambda_2^{\mathrm{n}} \right)}{\bar{\sigma}^{\mathrm{n}} \left(\Lambda_2^{\mathrm{n}} \right)^2}. \tag{2.38}$$

- Positive-electrode solid-potential TF is slightly different because of the sign change in the BC at $z = 0$.

$$\frac{\widetilde{\Phi}_{\mathrm{s}}^{\mathrm{p}}(z, s)}{I_{\mathrm{app}}(s)} = -\frac{1}{\bar{\sigma}^{\mathrm{p}}} \int_0^z \varepsilon_{\mathrm{s}}^{\mathrm{p}} A \frac{I_{\mathrm{s}}^{\mathrm{p}}(\zeta, s)}{I_{\mathrm{app}}(s)}\,\mathrm{d}\zeta$$

$$= \frac{z}{\bar{\sigma}^{\mathrm{p}}} + \frac{\mathrm{j}_1^{\mathrm{p}} \left(e^{\Lambda_1^{\mathrm{p}}(z-1)} - e^{-\Lambda_1^{\mathrm{p}}} - z\Lambda_1^{\mathrm{p}} e^{-\Lambda_1^{\mathrm{p}}} \right)}{\bar{\sigma}^{\mathrm{p}} \left(\Lambda_1^{\mathrm{p}} \right)^2} + \frac{\mathrm{j}_2^{\mathrm{p}} \left(e^{-\Lambda_1^{\mathrm{p}} z} - 1 + z\Lambda_1^{\mathrm{p}} \right)}{\bar{\sigma}^{\mathrm{p}} \left(\Lambda_1^{\mathrm{p}} \right)^2}$$

$$+ \frac{\mathrm{j}_3^{\mathrm{p}} \left(e^{\Lambda_2^{\mathrm{p}}(z-1)} - e^{-\Lambda_2^{\mathrm{p}}} - z\Lambda_2^{\mathrm{p}} e^{-\Lambda_2^{\mathrm{p}}} \right)}{\bar{\sigma}^{\mathrm{p}} \left(\Lambda_2^{\mathrm{p}} \right)^2} + \frac{\mathrm{j}_4^{\mathrm{p}} \left(e^{-\Lambda_2^{\mathrm{p}} z} - 1 + z\Lambda_2^{\mathrm{p}} \right)}{\bar{\sigma}^{\mathrm{p}} \left(\Lambda_2^{\mathrm{p}} \right)^2}. \tag{2.39}$$

Electrolyte potential transfer function

- We obtain a transfer function for the electrolyte potential by integrating Eq. (2.4) twice with respect to $\tilde{x}$.
- The ionic current flowing through the electrolyte is defined as:

$$\varepsilon_{\mathrm{e}} A i_{\mathrm{e}}(\tilde{x},t) = -\bar{\kappa}\frac{\partial \phi_{\mathrm{e}}(\tilde{x},t)}{\partial \tilde{x}} - \bar{\kappa}\bar{\kappa}_D T \frac{\partial \ln \theta_{\mathrm{e}}(\tilde{x},t)}{\partial \tilde{x}}.$$

- Hence, we can rewrite the electrolyte-potential PDE as:

$$\varepsilon_{\mathrm{e}} A \frac{\partial i_{\mathrm{e}}(\tilde{x},t)}{\partial \tilde{x}} = i_{\mathrm{f+dl}}(\tilde{x},t).$$

Negative electrode

- Transfer function for $i_{\mathrm{e}}(z,t)$ in the negative electrode is:

$$\begin{aligned}\varepsilon_{\mathrm{e}} A \frac{I_{\mathrm{e}}^{\mathrm{n}}(z,s)}{I_{\mathrm{app}}(s)} &= \int_0^z \frac{I_{\mathrm{f+dl}}^{\mathrm{r}}(\zeta,s)}{I_{\mathrm{app}}(s)}\,\mathrm{d}\zeta \\ &= \mathrm{j}_1^{\mathrm{n}} e^{-\Lambda_1^{\mathrm{n}}}\frac{e^{\Lambda_1^{\mathrm{n}} z}-1}{\Lambda_1^{\mathrm{n}}} - \mathrm{j}_2^{\mathrm{n}}\frac{e^{-\Lambda_1^{\mathrm{n}} z}-1}{\Lambda_1^{\mathrm{n}}} + \mathrm{j}_3^{\mathrm{n}} e^{-\Lambda_2^{\mathrm{n}}}\frac{e^{\Lambda_2^{\mathrm{n}} z}-1}{\Lambda_2^{\mathrm{n}}} - \mathrm{j}_4^{\mathrm{n}}\frac{e^{-\Lambda_2^{\mathrm{n}} z}-1}{\Lambda_2^{\mathrm{n}}}.\end{aligned}$$

- We now integrate again in order to find the electrolyte potential transfer function. That is, if we define $\tilde{\phi}_{\mathrm{e}}(\tilde{x},t) = \phi_{\mathrm{e}}(\tilde{x},t) - \phi_{\mathrm{e}}^{\mathrm{n}}(0,t)$, then:

$$\begin{aligned}\tilde{\phi}_{\mathrm{e}}^{\mathrm{n}}(z,t) &= -\frac{1}{\bar{\kappa}^{\mathrm{n}}}\int_0^z \varepsilon_{\mathrm{e}}^{\mathrm{n}} A i_{\mathrm{e}}^{\mathrm{n}}(\zeta,t)\,\mathrm{d}\zeta - \bar{\kappa}_D T \int_0^z \frac{\partial \ln \theta_{\mathrm{e}}^{\mathrm{n}}(\zeta,t)}{\partial \zeta}\,\mathrm{d}\zeta \\ &\approx \underbrace{-\frac{1}{\bar{\kappa}^{\mathrm{n}}}\int_0^z \varepsilon_{\mathrm{e}}^{\mathrm{n}} A i_{\mathrm{e}}^{\mathrm{n}}(\zeta,t)\,\mathrm{d}\zeta}_{\left[\tilde{\phi}_{\mathrm{e}}^{\mathrm{n}}(z,t)\right]_1} \underbrace{-\bar{\kappa}_D T \int_0^z \frac{\partial \tilde{\theta}_{\mathrm{e}}^{\mathrm{n}}(\zeta,t)}{\partial \zeta}\,\mathrm{d}\zeta}_{\left[\tilde{\phi}_{\mathrm{e}}^{\mathrm{n}}(z,t)\right]_2},\end{aligned} \tag{2.40}$$

where the natural log has been linearized by Taylor series.

- First, the transfer function for $\left[\tilde{\phi}_{\mathrm{e}}^{\mathrm{n}}(z,t)\right]_1$ will be:

$$\frac{\left[\widetilde{\Phi}_{\mathrm{e}}^{\mathrm{n}}(z,s)\right]_1}{I_{\mathrm{app}}(s)} = -\frac{1}{\bar{\kappa}^{\mathrm{n}}}\int_0^z \varepsilon_{\mathrm{e}} A \frac{I_{\mathrm{e}}^{\mathrm{n}}(\zeta,s)}{I_{\mathrm{app}}(s)}\,\mathrm{d}\zeta$$

$$= -\left(\frac{\mathrm{j}_1^{\mathrm{n}}\left(e^{\Lambda_1^{\mathrm{n}}(z-1)} - e^{-\Lambda_1^{\mathrm{n}}} - z\Lambda_1^{\mathrm{n}} e^{-\Lambda_1^{\mathrm{n}}}\right)}{\bar{\kappa}^{\mathrm{n}}\left(\Lambda_1^{\mathrm{n}}\right)^2} + \frac{\mathrm{j}_2^{\mathrm{n}}\left(e^{-\Lambda_1^{\mathrm{n}} z} - 1 + z\Lambda_1^{\mathrm{n}}\right)}{\bar{\kappa}^{\mathrm{n}}\left(\Lambda_1^{\mathrm{n}}\right)^2}\right.$$

$$\left. + \frac{\mathrm{j}_3^{\mathrm{n}}\left(e^{\Lambda_2^{\mathrm{n}}(z-1)} - e^{-\Lambda_2^{\mathrm{n}}} - z\Lambda_2^{\mathrm{n}} e^{-\Lambda_2^{\mathrm{n}}}\right)}{\bar{\kappa}^{\mathrm{n}}\left(\Lambda_2^{\mathrm{n}}\right)^2} + \frac{\mathrm{j}_4^{\mathrm{n}}\left(e^{-\Lambda_2^{\mathrm{n}} z} - 1 + z\Lambda_2^{\mathrm{n}}\right)}{\bar{\kappa}^{\mathrm{n}}\left(\Lambda_2^{\mathrm{n}}\right)^2}\right).$$

- The transfer function for the second term is:

$$\frac{\left[\widetilde{\Phi}_{\mathrm{e}}^{\mathrm{n}}(z,s)\right]_2}{I_{\mathrm{app}}(s)} = -\bar{\kappa}_D T \int_0^z \frac{\partial}{\partial\zeta}\frac{\widetilde{\Theta}_{\mathrm{e}}^{\mathrm{n}}(\zeta,s)}{I_{\mathrm{app}}(s)}\,\mathrm{d}\zeta$$

$$= -\bar{\kappa}_D T \int_0^z (c_1^{\mathrm{n}}\Lambda_1^{\mathrm{n}} e^{\Lambda_1^{\mathrm{n}}(\zeta-1)} - c_2^{\mathrm{n}}\Lambda_1^{\mathrm{n}} e^{-\Lambda_1^{\mathrm{n}}\zeta}$$

$$+ c_3^{\mathrm{n}}\Lambda_2^{\mathrm{n}} e^{\Lambda_2^{\mathrm{n}}(\zeta-1)} - c_4^{\mathrm{n}}\Lambda_2^{\mathrm{n}} e^{-\Lambda_2^{\mathrm{n}}\zeta})\,\mathrm{d}\zeta$$

$$= -\bar{\kappa}_D T \left(c_1^{\mathrm{n}}\left(e^{\Lambda_1^{\mathrm{n}}(z-1)} - e^{-\Lambda_1^{\mathrm{n}}}\right) + c_2^{\mathrm{n}}\left(e^{-\Lambda_1^{\mathrm{n}} z} - 1\right)\right.$$

$$\left. + c_3^{\mathrm{n}}\left(e^{\Lambda_2^{\mathrm{n}}(z-1)} - e^{-\Lambda_2^{\mathrm{n}}}\right) + c_4^{\mathrm{n}}\left(e^{-\Lambda_2^{\mathrm{n}} z} - 1\right)\right).$$

- Overall, electrolyte-potential TF in negative electrode is:

$$\frac{\widetilde{\Phi}_{\mathrm{e}}^{\mathrm{n}}(z,s)}{I_{\mathrm{app}}(s)} = \frac{\left[\widetilde{\Phi}_{\mathrm{e}}^{\mathrm{n}}(z,s)\right]_1}{I_{\mathrm{app}}(s)} + \frac{\left[\widetilde{\Phi}_{\mathrm{e}}^{\mathrm{n}}(z,s)\right]_2}{I_{\mathrm{app}}(s)}. \tag{2.41}$$

Separator region

- The transfer function for $i_{\mathrm{e}}(z,t)$ in the separator electrode is:

$$\varepsilon_e A \frac{I_{\rm e}^{\rm s}(z,s)}{I_{\rm app}(s)} = 1.$$

- We now integrate again (over the separator region only, for now) and use the same nomenclature as in Eq. (2.40).
- The transfer function for the first term is:

$$\frac{\left[\widetilde{\Phi}_{\rm e}^{\rm s}(z,s)\right]_1}{I_{\rm app}(s)} = -\frac{1}{\bar{\kappa}^{\rm s}} \int_0^z \varepsilon_{\rm e}^{\rm s} A \frac{I_{\rm e}^{\rm s}(\zeta,s)}{I_{\rm app}(s)}\,{\rm d}\zeta = -\frac{z}{\bar{\kappa}^{\rm s}}.$$

- The transfer function for the second term is:

$$\begin{aligned}\frac{\left[\widetilde{\Phi}_{\rm e}^{\rm s}(z,s)\right]_2}{I_{\rm app}(s)} &= -\bar{\kappa}_D T \int_0^z \frac{\partial}{\partial\zeta}\frac{\widetilde{\Theta}_{\rm e}^{\rm s}(\zeta,s)}{I_{\rm app}(s)}\,{\rm d}\zeta \\ &= -\bar{\kappa}_D T \int_0^z \left(c_1^{\rm s}\Lambda_1^{\rm s} e^{\Lambda_1^{\rm s}(\zeta-1)} - c_2^{\rm s}\Lambda_1^{\rm s} e^{-\Lambda_1^{\rm s}\zeta}\right){\rm d}\zeta \\ &= -\bar{\kappa}_D T \left(c_1^{\rm s}\left(e^{\Lambda_1^{\rm s}(z-1)} - e^{-\Lambda_1^{\rm s}}\right) + c_2^{\rm s}\left(e^{-\Lambda_1^{\rm s}z} - 1\right)\right).\end{aligned}$$

- The overall electrolyte potential transfer function in the separator region, now including the integral over the negative-electrode region, can be written:

$$\frac{\widetilde{\Phi}_{\rm e}^{\rm s}(z,s)}{I_{\rm app}(s)} = \frac{\widetilde{\Phi}_{\rm e}^{\rm n}(1,s)}{I_{\rm app}(s)} + \frac{\left[\widetilde{\Phi}_{\rm e}^{\rm s}(z,s)\right]_1}{I_{\rm app}(s)} + \frac{\left[\widetilde{\Phi}_{\rm e}^{\rm s}(z,s)\right]_2}{I_{\rm app}(s)}. \tag{2.42}$$

Positive electrode

- In the positive electrode,

$$\varepsilon_{\rm e}^{\rm p} A \frac{\partial I_{\rm e}^{\rm p}(\tilde{x},s)}{\partial\tilde{x}} = I_{\rm f+dl}^{\rm p}(\tilde{x},s).$$

- Integrating,

$$\varepsilon_{\mathrm{e}}^{\mathrm{p}} A \int_2^{\tilde{x}} \frac{\partial I_{\mathrm{e}}^{\mathrm{p}}(\xi, s)}{\partial \xi}\, \mathrm{d}\xi = \int_2^{\tilde{x}} I_{\mathrm{f+dl}}^{\mathrm{p}}(\xi, s)\, \mathrm{d}\xi$$

$$\varepsilon_{\mathrm{e}}^{\mathrm{p}} A \left[I_{\mathrm{e}}^{\mathrm{p}}(\tilde{x}, s) - I_{\mathrm{e}}^{\mathrm{p}}(2, s) \right] = \int_2^{\tilde{x}} I_{\mathrm{f+dl}}^{\mathrm{p}}(\xi, s)\, \mathrm{d}\xi$$

$$\varepsilon_{\mathrm{e}}^{\mathrm{p}} A I_{\mathrm{e}}^{\mathrm{p}}(\tilde{x}, s) - I_{\mathrm{app}}(s) = \int_2^{\tilde{x}} I_{\mathrm{f+dl}}^{\mathrm{p}}(\xi, s)\, \mathrm{d}\xi$$

$$\varepsilon_{\mathrm{e}}^{\mathrm{p}} A \frac{I_{\mathrm{e}}^{\mathrm{p}}(\tilde{x}, s)}{I_{\mathrm{app}}(s)} = 1 + \int_2^{\tilde{x}} \frac{I_{\mathrm{f+dl}}^{\mathrm{p}}(\xi, s)}{I_{\mathrm{app}}(s)}\, \mathrm{d}\xi.$$

- Changing variables, $z = 3 - \tilde{x}$, $\zeta = 3 - \xi$,

$$\varepsilon_{\mathrm{e}}^{\mathrm{p}} A \frac{I_{\mathrm{e}}^{\mathrm{p}}(z, s)}{I_{\mathrm{app}}(s)} = 1 - \int_1^{z} \frac{I_{\mathrm{f+dl}}^{\mathrm{p}}(\zeta, s)}{I_{\mathrm{app}}(s)}\, \mathrm{d}\zeta.$$

- So, the transfer function for $i_{\mathrm{e}}(z, t)$ in the positive electrode is:

$$\begin{aligned}
\varepsilon_{\mathrm{e}}^{\mathrm{p}} A \frac{I_{\mathrm{e}}^{\mathrm{p}}(z, t)}{I_{\mathrm{app}}(s)} &= 1 - \int_1^{z} \frac{I_{\mathrm{f+dl}}^{\mathrm{p}}(\zeta, s)}{I_{\mathrm{app}}(s)}\, \mathrm{d}\zeta \\
&= 1 + \left(\frac{\mathrm{j}_1^{\mathrm{p}}(e^{\Lambda_1^{\mathrm{p}}(z-1)} - 1)}{\Lambda_1^{\mathrm{p}}} - \frac{\mathrm{j}_2^{\mathrm{p}}(e^{-\Lambda_1^{\mathrm{p}} z} - e^{-\Lambda_1^{\mathrm{p}}})}{\Lambda_1^{\mathrm{p}}} \right. \\
&\quad \left. + \frac{\mathrm{j}_3^{\mathrm{p}}(e^{\Lambda_2^{\mathrm{p}}(z-1)} - 1)}{\Lambda_2^{\mathrm{p}}} - \frac{\mathrm{j}_4^{\mathrm{p}}(e^{-\Lambda_2^{\mathrm{p}} z} - e^{-\Lambda_2^{\mathrm{p}}})}{\Lambda_2^{\mathrm{p}}} \right).
\end{aligned}$$

- We now integrate again (over the positive-electrode region only, for now) and use the same nomenclature as in Eq. (2.40).

- The transfer function for the first term is:

$$\frac{\left[\widetilde{\Phi}_{\mathrm{e}}^{\mathrm{p}}(z, s)\right]_1}{I_{\mathrm{app}}(s)} = \frac{1}{\bar{\kappa}^{\mathrm{p}}} \int_1^{z} \varepsilon_{\mathrm{e}}^{\mathrm{p}} A \frac{I_{\mathrm{e}}^{\mathrm{p}}(\zeta, s)}{I_{\mathrm{app}}(s)}\, \mathrm{d}\zeta$$

$$= \frac{(z-1)}{\bar{\kappa}^{\mathrm{p}}} - \left(\frac{\mathrm{j}_1^{\mathrm{p}} \left(e^{\Lambda_1^{\mathrm{p}}(z-1)} + (1-z)\Lambda_1^{\mathrm{p}} - 1 \right)}{\bar{\kappa}^{\mathrm{p}} \left(\Lambda_1^{\mathrm{p}} \right)^2} \right.$$

$$+ \frac{\mathrm{j}_2^{\mathrm{p}} \left(e^{-\Lambda_1^{\mathrm{p}} z} + (z-1)\Lambda_1^{\mathrm{p}} e^{-\Lambda_1^{\mathrm{p}}} - e^{-\Lambda_1^{\mathrm{p}}} \right)}{\bar{\kappa}^{\mathrm{p}} \left(\Lambda_1^{\mathrm{p}} \right)^2}$$

$$+ \frac{\mathrm{j}_3^{\mathrm{p}} \left(e^{\Lambda_2^{\mathrm{p}}(z-1)} + (1-z)\Lambda_2^{\mathrm{p}} - 1 \right)}{\bar{\kappa}^{\mathrm{p}} \left(\Lambda_2^{\mathrm{p}} \right)^2}$$

$$\left. + \frac{\mathrm{j}_4^{\mathrm{p}} \left(e^{-\Lambda_2^{\mathrm{p}} z} + (z-1)\Lambda_2^{\mathrm{p}} e^{-\Lambda_2^{\mathrm{p}}} - e^{-\Lambda_2^{\mathrm{p}}} \right)}{\bar{\kappa}^{\mathrm{p}} \left(\Lambda_2^{\mathrm{p}} \right)^2} \right).$$

- The transfer function for the second term is:

$$\frac{\left[\widetilde{\Phi}_{\mathrm{e}}^{\mathrm{p}}(z,s)\right]_2}{I_{\mathrm{app}}(s)} = -\bar{\kappa}_D T \int_1^z \frac{\partial}{\partial \zeta} \frac{\widetilde{\Theta}_{\mathrm{e}}^{\mathrm{p}}(\zeta,s)}{I_{\mathrm{app}}(s)} \, \mathrm{d}\zeta$$

$$= -\bar{\kappa}_D T \int_1^z c_1^{\mathrm{p}} \Lambda_1^{\mathrm{p}} e^{\Lambda_1^{\mathrm{p}}(\zeta-1)} - c_2^{\mathrm{p}} \Lambda_1^{\mathrm{p}} e^{-\Lambda_1^{\mathrm{p}}(s)\zeta}$$

$$+ c_3^{\mathrm{p}} \Lambda_2^{\mathrm{p}} e^{\Lambda_2^{\mathrm{p}}(\zeta-1)} - c_4^{\mathrm{p}} \Lambda_2^{\mathrm{p}} e^{-\Lambda_2^{\mathrm{p}}\zeta} \, \mathrm{d}\zeta$$

$$= -\bar{\kappa}_D T \left(c_1^{\mathrm{p}} \left(e^{\Lambda_1^{\mathrm{p}}(z-1)} - 1 \right) + c_2^{\mathrm{p}} \left(e^{-\Lambda_1^{\mathrm{p}} z} - e^{-\Lambda_1^{\mathrm{p}}} \right) \right.$$

$$\left. + c_3^{\mathrm{p}} \left(e^{\Lambda_2^{\mathrm{p}}(z-1)} - 1 \right) + c_4^{\mathrm{p}} \left(e^{-\Lambda_2^{\mathrm{p}} z} - e^{-\Lambda_2^{\mathrm{p}}} \right) \right).$$

- Electrolyte-potential transfer function in positive electrode is therefore:

$$\frac{\widetilde{\Phi}_{\mathrm{e}}^{\mathrm{p}}(z,s)}{I_{\mathrm{app}}(s)} = \frac{\widetilde{\Phi}_{\mathrm{e}}^{\mathrm{s}}(1,s)}{I_{\mathrm{app}}(s)} + \frac{\left[\widetilde{\Phi}_{\mathrm{e}}^{\mathrm{p}}(z,s)\right]_1}{I_{\mathrm{app}}(s)} + \frac{\left[\widetilde{\Phi}_{\mathrm{e}}^{\mathrm{p}}(z,s)\right]_2}{I_{\mathrm{app}}(s)}. \tag{2.43}$$

Appendix 2.c: Closed-form solution for TF constants

- The coefficients of the electrolyte-concentration transfer function follow the relationship shown in the matrix form in App. 2.b.
- Can solve matrix equation numerically for every frequency of interest; alternately, can determine closed-form solution for all coefficients.
- This appendix gives the closed-form expressions, but omits the (very tedious, done by computer symbolic manipulation) algebra.
- To express the solution, we first define (for $\mathrm{r} \in \{\mathrm{n}, \mathrm{p}\}$)

$$\omega_+^{\mathrm{r}} = \bar{\kappa}^{\mathrm{s}} \Lambda_1^{\mathrm{s}} \left(\lambda_2^{\mathrm{r}} \coth(\Lambda_1^{\mathrm{r}}) - \lambda_1^{\mathrm{r}} \coth(\Lambda_2^{\mathrm{r}}) \right) + \bar{\kappa}^{\mathrm{r}} \left(\lambda_2^{\mathrm{r}} \Lambda_1^{\mathrm{r}} - \lambda_1^{\mathrm{r}} \Lambda_2^{\mathrm{r}} \right)$$

$$\omega_-^{\mathrm{r}} = \bar{\kappa}^{\mathrm{s}} \Lambda_1^{\mathrm{s}} \left(\lambda_2^{\mathrm{r}} \coth(\Lambda_1^{\mathrm{r}}) - \lambda_1^{\mathrm{r}} \coth(\Lambda_2^{\mathrm{r}}) \right) - \bar{\kappa}^{\mathrm{r}} \left(\lambda_2^{\mathrm{r}} \Lambda_1^{\mathrm{r}} - \lambda_1^{\mathrm{r}} \Lambda_2^{\mathrm{r}} \right)$$

$$\mathrm{den}^{\mathrm{r}} = \bar{\sigma}^{\mathrm{r}} \bar{\kappa}^{\mathrm{r}} \left(\omega_-^{\mathrm{n}} \omega_-^{\mathrm{p}} e^{-2\Lambda_1^{\mathrm{s}}} - \omega_+^{\mathrm{n}} \omega_+^{\mathrm{p}} \right).$$

- Then, the electrolyte-concentration transfer-function coefficients for the separator region are:

$$c_1^{\mathrm{s}} = -\frac{\bar{\kappa}^{\mathrm{n}} \mu_1^{\mathrm{n}} \omega_-^{\mathrm{p}} e^{-\Lambda_1^{\mathrm{s}}}}{\mathrm{den}^{\mathrm{n}}} \left[\bar{\sigma}^{\mathrm{n}} \left\{ \Lambda_2^{\mathrm{n}} \coth(\Lambda_1^{\mathrm{n}}) - \Lambda_1^{\mathrm{n}} \coth(\Lambda_2^{\mathrm{n}}) \right\} \right.$$
$$\left. + \bar{\kappa}^{\mathrm{n}} \left\{ \Lambda_2^{\mathrm{n}} \mathrm{csch}(\Lambda_1^{\mathrm{n}}) - \Lambda_1^{\mathrm{n}} \mathrm{csch}(\Lambda_2^{\mathrm{n}}) \right\} \right]$$
$$+ \frac{\bar{\kappa}^{\mathrm{p}} \mu_1^{\mathrm{p}} \omega_+^{\mathrm{n}}}{\mathrm{den}^{\mathrm{p}}} \left[\bar{\sigma}^{\mathrm{p}} \left\{ \Lambda_2^{\mathrm{p}} \coth(\Lambda_1^{\mathrm{p}}) - \Lambda_1^{\mathrm{p}} \coth(\Lambda_2^{\mathrm{p}}) \right\} \right.$$
$$\left. + \bar{\kappa}^{\mathrm{p}} \left\{ \Lambda_2^{\mathrm{p}} \mathrm{csch}(\Lambda_1^{\mathrm{p}}) - \Lambda_1^{\mathrm{p}} \mathrm{csch}(\Lambda_2^{\mathrm{p}}) \right\} \right]$$

$$c_2^{\mathrm{s}} = -\frac{\bar{\kappa}^{\mathrm{n}} \mu_1^{\mathrm{n}} \omega_+^{\mathrm{p}}}{\mathrm{den}^{\mathrm{n}}} \left[\bar{\sigma}^{\mathrm{n}} \left\{ \Lambda_2^{\mathrm{n}} \coth(\Lambda_1^{\mathrm{n}}) - \Lambda_1^{\mathrm{n}} \coth(\Lambda_2^{\mathrm{n}}) \right\} \right.$$
$$\left. + \bar{\kappa}^{\mathrm{n}} \left\{ \Lambda_2^{\mathrm{n}} \mathrm{csch}(\Lambda_1^{\mathrm{n}}) - \Lambda_1^{\mathrm{n}} \mathrm{csch}(\Lambda_2^{\mathrm{n}}) \right\} \right]$$

$$+\frac{\bar{\kappa}^{\mathrm{p}}\mu_1^{\mathrm{p}}\omega_-^{\mathrm{n}}e^{-\Lambda_1^{\mathrm{s}}}}{\mathrm{den}^{\mathrm{p}}}\left[\bar{\sigma}^{\mathrm{p}}\left\{\Lambda_2^{\mathrm{p}}\coth(\Lambda_1^{\mathrm{p}})-\Lambda_1^{\mathrm{p}}\coth(\Lambda_2^{\mathrm{p}})\right\}\right.$$

$$\left.+\bar{\kappa}^{\mathrm{p}}\left\{\Lambda_2^{\mathrm{p}}\mathrm{csch}(\Lambda_1^{\mathrm{p}})-\Lambda_1^{\mathrm{p}}\mathrm{csch}(\Lambda_2^{\mathrm{p}})\right\}\right].$$

- Coefficients for electrode regions are expressed in terms of c_1^{s} and c_2^{s}.
- Negative-electrode region electrolyte-concentration TF coefficients:

$$c_1^{\mathrm{n}}=\frac{(1-e^{-2\Lambda_1^{\mathrm{n}}})^{-1}}{\bar{\kappa}^{\mathrm{n}}\left(\lambda_2^{\mathrm{n}}\Lambda_1^{\mathrm{n}}-\lambda_1^{\mathrm{n}}\Lambda_2^{\mathrm{n}}\right)}\left[\mu_1^{\mathrm{n}}\Lambda_2^{\mathrm{n}}\left(1+\frac{\bar{\kappa}^{\mathrm{n}}e^{-\Lambda_1^{\mathrm{n}}}}{\bar{\sigma}^{\mathrm{n}}}\right)+\bar{\kappa}^{\mathrm{s}}\Lambda_1^{\mathrm{s}}\lambda_2^{\mathrm{n}}\left(c_1^{\mathrm{s}}e^{-\Lambda_1^{\mathrm{s}}}-c_2^{\mathrm{s}}\right)\right]$$

$$c_2^{\mathrm{n}}=\frac{\mathrm{csch}(\Lambda_1^{\mathrm{n}})/2}{\bar{\kappa}^{\mathrm{n}}\left(\lambda_2^{\mathrm{n}}\Lambda_1^{\mathrm{n}}-\lambda_1^{\mathrm{n}}\Lambda_2^{\mathrm{n}}\right)}\left[\mu_1^{\mathrm{n}}\Lambda_2^{\mathrm{n}}\left(1+\frac{\bar{\kappa}^{\mathrm{n}}e^{\Lambda_1^{\mathrm{n}}}}{\bar{\sigma}^{\mathrm{n}}}\right)+\bar{\kappa}^{\mathrm{s}}\Lambda_1^{\mathrm{s}}\lambda_2^{\mathrm{n}}\left(c_1^{\mathrm{s}}e^{-\Lambda_1^{\mathrm{s}}}-c_2^{\mathrm{s}}\right)\right]$$

$$c_3^{\mathrm{n}}=\frac{-(1-e^{-2\Lambda_2^{\mathrm{n}}})^{-1}}{\bar{\kappa}^{\mathrm{n}}\left(\lambda_2^{\mathrm{n}}\Lambda_1^{\mathrm{n}}-\lambda_1^{\mathrm{n}}\Lambda_2^{\mathrm{n}}\right)}\left[\mu_1^{\mathrm{n}}\Lambda_1^{\mathrm{n}}\left(1+\frac{\bar{\kappa}^{\mathrm{n}}e^{-\Lambda_2^{\mathrm{n}}}}{\bar{\sigma}^{\mathrm{n}}}\right)+\bar{\kappa}^{\mathrm{s}}\Lambda_1^{\mathrm{s}}\lambda_1^{\mathrm{n}}\left(c_1^{\mathrm{s}}e^{-\Lambda_1^{\mathrm{s}}}-c_2^{\mathrm{s}}\right)\right]$$

$$c_4^{\mathrm{n}}=\frac{-\mathrm{csch}(\Lambda_2^{\mathrm{n}})/2}{\bar{\kappa}^{\mathrm{n}}\left(\lambda_2^{\mathrm{n}}\Lambda_1^{\mathrm{n}}-\lambda_1^{\mathrm{n}}\Lambda_2^{\mathrm{n}}\right)}\left[\mu_1^{\mathrm{n}}\Lambda_1^{\mathrm{n}}\left(1+\frac{\bar{\kappa}^{\mathrm{n}}e^{\Lambda_2^{\mathrm{n}}}}{\bar{\sigma}^{\mathrm{n}}}\right)+\bar{\kappa}^{\mathrm{s}}\Lambda_1^{\mathrm{s}}\lambda_1^{\mathrm{n}}\left(c_1^{\mathrm{s}}e^{-\Lambda_1^{\mathrm{s}}}-c_2^{\mathrm{s}}\right)\right].$$

- Positive-electrode region electrolyte-concentration TF coefficients:

$$c_1^{\mathrm{p}}=\frac{-(1-e^{-2\Lambda_1^{\mathrm{p}}})^{-1}}{\bar{\kappa}^{\mathrm{p}}\left(\lambda_2^{\mathrm{p}}\Lambda_1^{\mathrm{p}}-\lambda_1^{\mathrm{p}}\Lambda_2^{\mathrm{p}}\right)}\left[\mu_1^{\mathrm{p}}\Lambda_2^{\mathrm{p}}\left(1+\frac{\bar{\kappa}^{\mathrm{p}}e^{-\Lambda_1^{\mathrm{p}}}}{\bar{\sigma}^{\mathrm{p}}}\right)+\bar{\kappa}^{\mathrm{s}}\Lambda_1^{\mathrm{s}}\lambda_2^{\mathrm{p}}\left(c_1^{\mathrm{s}}-c_2^{\mathrm{s}}e^{-\Lambda_1^{\mathrm{s}}}\right)\right]$$

$$c_2^{\mathrm{p}}=\frac{-\mathrm{csch}(\Lambda_1^{\mathrm{p}})/2}{\bar{\kappa}^{\mathrm{p}}\left(\lambda_2^{\mathrm{p}}\Lambda_1^{\mathrm{p}}-\lambda_1^{\mathrm{p}}\Lambda_2^{\mathrm{p}}\right)}\left[\mu_1^{\mathrm{p}}\Lambda_2^{\mathrm{p}}\left(1+\frac{\bar{\kappa}^{\mathrm{p}}e^{\Lambda_1^{\mathrm{p}}}}{\bar{\sigma}^{\mathrm{p}}}\right)+\bar{\kappa}^{\mathrm{s}}\Lambda_1^{\mathrm{s}}\lambda_2^{\mathrm{p}}\left(c_1^{\mathrm{s}}-c_2^{\mathrm{s}}e^{-\Lambda_1^{\mathrm{s}}}\right)\right]$$

$$c_3^{\mathrm{p}}=\frac{(1-e^{-2\Lambda_2^{\mathrm{p}}})^{-1}}{\bar{\kappa}^{\mathrm{p}}\left(\lambda_2^{\mathrm{p}}\Lambda_1^{\mathrm{p}}-\lambda_1^{\mathrm{p}}\Lambda_2^{\mathrm{p}}\right)}\left[\mu_1^{\mathrm{p}}\Lambda_1^{\mathrm{p}}\left(1+\frac{\bar{\kappa}^{\mathrm{p}}e^{-\Lambda_2^{\mathrm{p}}}}{\bar{\sigma}^{\mathrm{p}}}\right)+\bar{\kappa}^{\mathrm{s}}\Lambda_1^{\mathrm{s}}\lambda_1^{\mathrm{p}}\left(c_1^{\mathrm{s}}-c_2^{\mathrm{s}}e^{-\Lambda_1^{\mathrm{s}}}\right)\right]$$

$$c_4^{\mathrm{p}}=\frac{\mathrm{csch}(\Lambda_2^{\mathrm{p}})/2}{\bar{\kappa}^{\mathrm{p}}\left(\lambda_2^{\mathrm{p}}\Lambda_1^{\mathrm{p}}-\lambda_1^{\mathrm{p}}\Lambda_2^{\mathrm{p}}\right)}\left[\mu_1^{\mathrm{p}}\Lambda_1^{\mathrm{p}}\left(1+\frac{\bar{\kappa}^{\mathrm{p}}e^{\Lambda_2^{\mathrm{p}}}}{\bar{\sigma}^{\mathrm{p}}}\right)+\bar{\kappa}^{\mathrm{s}}\Lambda_1^{\mathrm{s}}\lambda_1^{\mathrm{p}}\left(c_1^{\mathrm{s}}-c_2^{\mathrm{s}}e^{-\Lambda_1^{\mathrm{s}}}\right)\right].$$

Appendix 2.d: "Old-style" transfer functions

- This appendix lists transfer functions derived using Assumption **A2** but using lumped parameters and generalized interface model.

Negative-electrode transfer functions

- Following ECE5710 derivation procedure, but with lumped-parameter equations and new interface model we find dimensionless variable:

$$\nu^{\mathrm{n}}(s) = \sqrt{\frac{1}{\bar{\sigma}^{\mathrm{n}}} + \frac{1}{\bar{\kappa}^{\mathrm{n}}}} \Bigg/ \sqrt{\bar{Z}^{\mathrm{n}}_{\widetilde{\mathrm{se}}}(s)}.$$

- Note that $(\nu^{\mathrm{n}}(s))^2$ is a (unitless) ratio of impedances with exactly the same meaning as before:
  - Numerator is parallel impedance to electronic and ionic current of solid and electrolyte in x dimension
  - Denominator is impedance across solid–electrolyte boundary and due to diffusion in r dimension.
- We find the phase potential difference transfer function in the negative electrode to be:

$$\frac{\widetilde{\Phi}^{\mathrm{n}}_{\text{s-e}}(z,s)}{I_{\mathrm{app}}(s)} = \frac{[\bar{\sigma}^{\mathrm{n}}\cosh(\nu^{\mathrm{n}}(s)z) + \bar{\kappa}^{\mathrm{n}}\cosh(\nu^{\mathrm{n}}(s)(z-1))]}{\bar{\sigma}^{\mathrm{n}}\bar{\kappa}^{\mathrm{n}}\nu^{\mathrm{n}}(s)\sinh(\nu^{\mathrm{n}}(s))}.$$

- Interfacial lithium flux in negative electrode is:

$$\frac{I^{\mathrm{n}}_{\mathrm{f+dl}}(z,s)}{I_{\mathrm{app}}(s)} = \nu^{\mathrm{n}}(s)\frac{\bar{\sigma}^{\mathrm{n}}\cosh(\nu^{\mathrm{n}}(s)z) + \bar{\kappa}^{\mathrm{n}}\cosh(\nu^{\mathrm{n}}(s)(z-1))}{(\bar{\kappa}^{\mathrm{n}} + \bar{\sigma}^{\mathrm{n}})\sinh(\nu^{\mathrm{n}}(s))}.$$

- Solid surface concentration can be found just as for the new model,

$$\frac{\widetilde{\Theta}^{\mathrm{n}}_{\mathrm{ss}}(z,s)}{I_{\mathrm{app}}(s)} = \frac{\bar{Z}^{\mathrm{n}}_{\widetilde{\mathrm{s}}}(s)}{[U^{\mathrm{n}}_{\mathrm{ocp}}]'}\frac{\bar{Z}^{\mathrm{n}}_{\widetilde{\mathrm{dl}}}(s)}{\bar{R}^{\mathrm{n}}_{\mathrm{ct}} + \bar{Z}^{\mathrm{n}}_{\widetilde{\mathrm{s}}}(s) + \bar{Z}^{\mathrm{n}}_{\widetilde{\mathrm{dl}}}(s)}\frac{I^{\mathrm{n}}_{\mathrm{f+dl}}(z,s)}{I_{\mathrm{app}}(s)}.$$

- Solid potential in the negative electrode is:

$$\frac{\widetilde{\Phi}_s^{\mathrm{n}}(z,s)}{I_{\mathrm{app}}(s)} = -\left[\frac{\bar{\kappa}^{\mathrm{n}}\left(\cosh(\nu^{\mathrm{n}}(s)) - \cosh((z-1)\nu^{\mathrm{n}}(s))\right)}{\bar{\sigma}^{\mathrm{n}}(\bar{\kappa}^{\mathrm{n}}+\bar{\sigma}^{\mathrm{n}})\nu^{\mathrm{n}}(s)\sinh(\nu^{\mathrm{n}}(s))}\right.$$
$$\left. + \frac{\bar{\sigma}^{\mathrm{n}}\left(1 - \cosh(z\nu^{\mathrm{n}}(s)) + z\nu^{\mathrm{n}}(s)\sinh(\nu^{\mathrm{n}}(s))\right)}{\bar{\sigma}^{\mathrm{n}}(\bar{\kappa}^{\mathrm{n}}+\bar{\sigma}^{\mathrm{n}})\nu^{\mathrm{n}}(s)\sinh(\nu^{\mathrm{n}}(s))}\right].$$

Positive-electrode transfer functions

- In the positive electrode, the impedance ratio changes:

$$\nu^{\mathrm{p}}(s) = \sqrt{\frac{1}{\bar{\sigma}^{\mathrm{p}}} + \frac{1}{\bar{\kappa}^{\mathrm{p}}}} \Big/ \sqrt{\bar{Z}^{\mathrm{p}}_{\mathrm{s,e}}(s)}.$$

- The other transfer functions are simply multiplied by -1, but retain the same form.
- We find the phase potential difference transfer function in the positive electrode to be:

$$\frac{\widetilde{\Phi}^{\mathrm{p}}_{\mathrm{s\text{-}e}}(z,s)}{I_{\mathrm{app}}(s)} = -\frac{[\bar{\sigma}^{\mathrm{p}}\cosh(\nu^{\mathrm{p}}(s)z) + \bar{\kappa}^{\mathrm{p}}\cosh(\nu^{\mathrm{p}}(s)(z-1))]}{\bar{\sigma}^{\mathrm{p}}\bar{\kappa}^{\mathrm{p}}\nu^{\mathrm{p}}(s)\sinh(\nu^{\mathrm{p}}(s))}.$$

- Interfacial lithium flux in positive electrode is:

$$\frac{I^{\mathrm{p}}_{\mathrm{f+dl}}(z,s)}{I_{\mathrm{app}}(s)} = -\nu^{\mathrm{p}}(s)\frac{\bar{\sigma}^{\mathrm{p}}\cosh(\nu^{\mathrm{p}}(s)z) + \bar{\kappa}^{\mathrm{p}}\cosh(\nu^{\mathrm{p}}(s)(z-1))}{(\bar{\kappa}^{\mathrm{p}}+\bar{\sigma}^{\mathrm{p}})\sinh(\nu^{\mathrm{p}}(s))}.$$

- Solid surface concentration can be found just as for the new model,

$$\frac{\widetilde{\Theta}^{\mathrm{p}}_{\mathrm{ss}}(z,s)}{I_{\mathrm{app}}(s)} = \frac{\bar{Z}^{\mathrm{p}}_{\tilde{\mathrm{s}}}(s)}{[U^{\mathrm{p}}_{\mathrm{ocp}}]'}\frac{\bar{Z}^{\mathrm{p}}_{\widetilde{\mathrm{dl}}}(s)}{\bar{R}^{\mathrm{p}}_{\mathrm{ct}} + \bar{Z}^{\mathrm{p}}_{\tilde{\mathrm{s}}}(s) + \bar{Z}^{\mathrm{p}}_{\widetilde{\mathrm{dl}}}(s)}\frac{I^{\mathrm{p}}_{\mathrm{f+dl}}(z,s)}{I_{\mathrm{app}}(s)}.$$

- Solid potential in the positive electrode is:

$$\frac{\widetilde{\Phi}^{\mathrm{p}}_{\mathrm{s}}(z,s)}{I_{\mathrm{app}}(s)} = \left[\frac{\bar{\kappa}^{\mathrm{p}}\left(\cosh(\nu^{\mathrm{p}}(s)) - \cosh((z-1)\nu^{\mathrm{p}}(s))\right)}{\bar{\sigma}^{\mathrm{n}}(\bar{\kappa}^{\mathrm{p}}+\bar{\sigma}^{\mathrm{p}})\nu^{\mathrm{p}}(s)\sinh(\nu^{\mathrm{p}}(s))}\right.$$
$$\left. + \frac{\bar{\sigma}^{\mathrm{p}}\left(1 - \cosh(z\nu^{\mathrm{p}}(s)) + z\nu^{\mathrm{p}}(s)\sinh(\nu^{\mathrm{p}}(s))\right)}{\bar{\sigma}^{\mathrm{p}}(\bar{\kappa}^{\mathrm{p}}+\bar{\sigma}^{\mathrm{p}})\nu^{\mathrm{p}}(s)\sinh(\nu^{\mathrm{p}}(s))}\right].$$

Electrolyte-concentration transfer function

- The electrolyte-concentration transfer function can be found in a simpler manner than introduced in ECE5710.[18]
- The solution can be expressed in terms $\cosh(\cdot)$ and $\sinh(\cdot)$ basis functions, or in terms of exponentials.
- We find the exponential form to have somewhat better numeric stability at high frequencies, so I present that form here:

$$\frac{\widetilde{\Theta}_{\mathrm{e}}^{\mathrm{n}}(z,s)}{I_{\mathrm{app}}(s)} = c_1^{\mathrm{n}} \exp(\gamma^{\mathrm{n}}(s)z) + c_2^{\mathrm{n}} \exp(-\gamma^{\mathrm{n}}(s)z) + \alpha^{\mathrm{n}}(s)\frac{I_{\mathrm{f+dl}}^{\mathrm{n}}(z,s)}{I_{\mathrm{app}}(s)}$$

$$\frac{\widetilde{\Theta}_{\mathrm{e}}^{\mathrm{s}}(z,s)}{I_{\mathrm{app}}(s)} = c_1^{\mathrm{s}} \exp(\gamma^{\mathrm{s}}(s)z) + c_2^{\mathrm{s}} \exp(-\gamma^{\mathrm{s}}(s)z)$$

$$\frac{\widetilde{\Theta}_{\mathrm{e}}^{\mathrm{p}}(z,s)}{I_{\mathrm{app}}(s)} = c_1^{\mathrm{p}} \exp(\gamma^{\mathrm{p}}(s)z) + c_2^{\mathrm{p}} \exp(-\gamma^{\mathrm{p}}(s)z) + \alpha^{\mathrm{p}}(s)\frac{I_{\mathrm{f+dl}}^{\mathrm{p}}(z,s)}{I_{\mathrm{app}}(s)}.$$

- In this solution, we have defined:

$$\gamma^{\mathrm{r}}(s) = \sqrt{\frac{3600\bar{q}_{\mathrm{e}}^{\mathrm{r}}s}{\bar{\kappa}^{\mathrm{r}}\bar{\psi}}} \quad \text{and} \quad \alpha^{\mathrm{r}}(s) = \frac{-1}{\bar{\kappa}^{\mathrm{r}}\bar{\psi}((\nu^{\mathrm{r}}(s))^2 - (\gamma^{\mathrm{r}}(s))^2)}.$$

- Unknown constants determined by PDE BCs.
- These constants can be computed by solving a matrix equation where:

$$b_1 = \frac{\alpha^{\mathrm{n}}(s)}{\gamma^{\mathrm{n}}(s)}\left(\frac{(\nu^{\mathrm{n}}(s))^2\bar{\kappa}^{\mathrm{n}}}{\bar{\sigma}^{\mathrm{n}} + \bar{\kappa}^{\mathrm{n}}}\right) \qquad b_4 = -\frac{\alpha^{\mathrm{p}}(s)}{\gamma^{\mathrm{p}}(s)}\left(\frac{(\nu^{\mathrm{p}}(s))^2\bar{\kappa}^{\mathrm{p}}}{\bar{\sigma}^{\mathrm{p}} + \bar{\kappa}^{\mathrm{p}}}\right)$$

[18] Rodríguez, A., Plett, G.L., and Trimboli, M.S., "Fast computation of the electrolyte-concentration transfer function of a lithium-ion cell model", *J. Power Sources*, 360, 2017, 642–5.

$$b_2 = -\frac{\alpha^{\mathrm{n}}(s)}{\gamma^{\mathrm{n}}(s)}\left(\frac{(\nu^{\mathrm{n}}(s))^2\bar{\sigma}^{\mathrm{n}}}{\bar{\sigma}^{\mathrm{n}}+\bar{\kappa}^{\mathrm{n}}}\right) \qquad b_5 = -\alpha^{\mathrm{n}}\left(\frac{\nu^{\mathrm{n}}(s)(\bar{\kappa}^{\mathrm{n}}+\bar{\sigma}^{\mathrm{n}}\cosh(\nu^{\mathrm{n}}(s))}{(\bar{\sigma}^{\mathrm{n}}+\bar{\kappa}^{\mathrm{n}})\sinh(\nu^{\mathrm{n}}(s))}\right)$$

$$b_3 = \frac{\alpha^{\mathrm{p}}(s)}{\gamma^{\mathrm{p}}(s)}\left(\frac{(\nu^{\mathrm{p}}(s))^2\bar{\sigma}^{\mathrm{p}}}{\bar{\sigma}^{\mathrm{p}}+\bar{\kappa}^{\mathrm{p}}}\right) \qquad b_6 = -\alpha^{\mathrm{p}}\left(\frac{\nu^{\mathrm{p}}(s)(\bar{\kappa}^{\mathrm{p}}+\bar{\sigma}^{\mathrm{p}}\cosh(\nu^{\mathrm{p}}(s))}{(\bar{\sigma}^{\mathrm{p}}+\bar{\kappa}^{\mathrm{p}})\sinh(\nu^{\mathrm{p}}(s))}\right).$$

and

$$\begin{bmatrix} c_1^{\mathrm{n}} \\ c_2^{\mathrm{n}} \\ c_1^{\mathrm{s}} \\ c_2^{\mathrm{s}} \\ c_1^{\mathrm{p}} \\ c_2^{\mathrm{p}} \end{bmatrix} = \begin{bmatrix} 1 & -1 & 0 & 0 & 0 & 0 \\ e^{\gamma^{\mathrm{n}}} & -e^{-\gamma^{\mathrm{n}}} & -\dfrac{\bar{\kappa}^{\mathrm{s}}\gamma^{\mathrm{s}}}{\bar{\kappa}^{\mathrm{n}}\gamma^{\mathrm{n}}} & \dfrac{\bar{\kappa}^{\mathrm{s}}\gamma^{\mathrm{s}}}{\bar{\kappa}^{\mathrm{n}}\gamma^{\mathrm{n}}} & 0 & 0 \\ 0 & 0 & \dfrac{\bar{\kappa}^{\mathrm{s}}\gamma^{\mathrm{s}}}{\bar{\kappa}^{\mathrm{p}}\gamma^{\mathrm{p}}}e^{\gamma^{\mathrm{s}}} & -\dfrac{\bar{\kappa}^{\mathrm{s}}\gamma^{\mathrm{s}}}{\bar{\kappa}^{\mathrm{p}}\gamma^{\mathrm{p}}}e^{-\gamma^{\mathrm{s}}} & e^{\gamma^{\mathrm{p}}} & -e^{-\gamma^{\mathrm{p}}} \\ 0 & 0 & 0 & 0 & 1 & -1 \\ e^{\gamma^{\mathrm{n}}} & e^{-\gamma^{\mathrm{n}}} & -1 & -1 & 0 & 0 \\ 0 & 0 & e^{\gamma^{\mathrm{s}}} & e^{-\gamma^{\mathrm{s}}} & -e^{\gamma^{\mathrm{p}}} & -e^{-\gamma^{\mathrm{p}}} \end{bmatrix}^{-1} \begin{bmatrix} b_1 \\ b_2 \\ b_3 \\ b_4 \\ b_5 \\ b_6 \end{bmatrix},$$

- This matrix equation can be solved analytically by manual back-substitution. For brevity, we omit that derivation here.

Electrolyte-potential transfer function

- Define $\tilde{\phi}_e(x,t) = \phi_e(x,t) - \phi_e(0,t)$.
- Then, $\tilde{\phi}_e(x,t)$ comprises two parts:
  - The first part, $\left[\tilde{\phi}_e(x,t)\right]_1$, can be determined via transfer functions
  - The second part, $\left[\tilde{\phi}_e(x,t)\right]_2$, can be determined via known $c_e(x,t)$.
- In the negative electrode,

$$\frac{[\widetilde{\Phi}_{\mathrm{e}}^{\mathrm{n}}(z,s)]_1}{I_{\mathrm{app}}(s)} = -\frac{\bar{\sigma}^{\mathrm{n}}\left(\cosh\left(z\nu^{\mathrm{n}}(s)\right)-1\right)}{\bar{\kappa}^{\mathrm{n}}(\bar{\kappa}^{\mathrm{n}}+\bar{\sigma}^{\mathrm{n}})\nu^{\mathrm{n}}(s)\sinh(\nu^{\mathrm{n}}(s))} - \frac{z}{\bar{\kappa}^{\mathrm{n}}+\bar{\sigma}^{\mathrm{n}}} - \frac{\left(\cosh\left(\nu^{\mathrm{n}}(s)(1-z)\right)-\cosh(\nu^{\mathrm{n}}(s))\right)}{(\bar{\kappa}^{\mathrm{n}}+\bar{\sigma}^{\mathrm{n}})\nu^{\mathrm{n}}(s)\sinh(\nu^{\mathrm{n}}(s))}.$$

- In the separator, we then have:

$$\frac{[\widetilde{\Phi}_{\rm e}^{\rm s}(z,s)]_1}{I_{\rm app}(s)} = -\frac{\left((\bar{\sigma}^{\rm n}-\bar{\kappa}^{\rm n})\tanh\left(\frac{\nu^{\rm n}(s)}{2}\right)\right)}{\bar{\kappa}^{\rm n}(\bar{\kappa}^{\rm n}+\bar{\sigma}^{\rm n})\nu^{\rm n}(s)} - \frac{1}{\bar{\kappa}^{\rm n}+\bar{\sigma}^{\rm n}} - \frac{z}{\bar{\kappa}^{\rm s}}.$$

- In the positive electrode, we then have:

$$\begin{aligned}\frac{[\widetilde{\Phi}_{\rm e}^{\rm p}(z,s)]_1}{I_{\rm app}(s)} = &\frac{\left((\bar{\kappa}^{\rm n}-\bar{\sigma}^{\rm n})\tanh\left(\frac{\nu^{\rm n}(s)}{2}\right)-\bar{\kappa}^{\rm n}\nu^{\rm n}(s)\right)}{\bar{\kappa}^{\rm n}(\bar{\kappa}^{\rm n}+\bar{\sigma}^{\rm n})\nu^{\rm n}(s)} - \frac{1}{\bar{\kappa}^{\rm s}} \\ &- \frac{\bar{\sigma}^{\rm p}\left(\cosh\left(\nu^{\rm p}(s)\right)-\cosh\left(\nu^{\rm p}(s)z\right)\right)}{\bar{\kappa}^{\rm p}(\bar{\kappa}^{\rm p}+\bar{\sigma}^{\rm p})\nu^{\rm p}(s)\sinh(\nu^{\rm p}(s))} \\ &- \frac{\left(1-\cosh\left(\nu^{\rm p}(s)(z-1)\right)\right)}{(\bar{\kappa}^{\rm p}+\bar{\sigma}^{\rm p})\nu^{\rm p}(s)\sinh(\nu^{\rm p}(s))} + \frac{z-1}{\bar{\kappa}^{\rm p}+\bar{\sigma}^{\rm p}}.\end{aligned}$$

- The second term of $\tilde{\phi}_{\rm e}^{\rm r}(z,t)$ is found in the time domain:

$$\left[\tilde{\phi}_{\rm e}^{\rm r}(z,t)\right]_2 = -\bar{\kappa}_D T\,\ln\tilde{\theta}_{\rm e}(z,t).$$

- To compute $\tilde{\phi}_{\rm e}^{\rm r}(z,t)$, we must compute its two parts and add them.

Appendix 2.e: Transfer-function limits

- We will need closed-form solutions for integrator residues and low-frequency (LF, $s \to 0$) and high-frequency (HF, $s \to \infty$) TF responses.
- This appendix summarizes those results.

Integrator residues

- During ROM generation process described in Ch. 4, we must remove integrator dynamics from all TFs (then add back in later).
- Integrator residue of TF $G(s)$ is defined as $\text{res}_0^{\text{r}} = \lim_{s\to 0} sG^{\text{r}}(s)$. Then...

ELECTROLYTE CONCENTRATION: The $\widetilde{\Theta}_{\text{e}}^{\text{r}}(\tilde{x}, s)/I_{\text{app}}(s)$ TFs do not have integrators. So, $\text{res}_0^{\text{r}} = 0$.

SOLID SURFACE CONCENTRATION: The LF behavior of $\widetilde{\Theta}_{\text{ss}}^{\text{r}}(\tilde{x}, s)/I_{\text{app}}(s)$ has integration dynamics. For the case of CPE, we define $\bar{C}_{\text{dl,eff}}^{\text{r}} = \left(\bar{C}_{\text{dl}}\right)^{2-n_{\text{dl}}^{\text{r}}} (\omega_{\text{dl}})^{n_{\text{dl}}^{\text{r}}-1}$. Then, the negative- and positive-electrode residues are:

$$\text{res}_0^{\text{n}} = -\frac{\left|\theta_{100}^{\text{n}} - \theta_0^{\text{n}}\right|}{3600Q - \bar{C}_{\text{dl,eff}}^{\text{n}} \left|\theta_{100}^{\text{n}} - \theta_0^{\text{n}}\right| \; [U_{\text{ocp}}^{\text{n}}]'}$$

$$\text{res}_0^{\text{p}} = \frac{\left|\theta_{100}^{\text{p}} - \theta_0^{\text{p}}\right|}{3600Q - \bar{C}_{\text{dl,eff}}^{\text{p}} \left|\theta_{100}^{\text{p}} - \theta_0^{\text{p}}\right| \; [U_{\text{ocp}}^{\text{p}}]'}.$$

The corresponding integrator-removed TFs are:

$$\frac{[\widetilde{\Theta}_{\text{ss}}^{\text{r}}(\tilde{x}, s)]^*}{I_{\text{app}}(s)} = \frac{\widetilde{\Theta}_{\text{ss}}^{\text{r}}(\tilde{x}, s)}{I_{\text{app}}(s)} - \frac{\text{res}_0^{\text{r}}}{s}.$$

ELECTROLYTE POTENTIAL: $\widetilde{\Phi}_{\text{e}}^{\text{r}}(\tilde{x}, s)/I_{\text{app}}(s)$ has no integrators: $\text{res}_0^{\text{r}} = 0$.

SOLID POTENTIAL: The $\widetilde{\Phi}_{\text{s}}^{\text{r}}(\tilde{x}, s)/I_{\text{app}}(s)$ has no integrators. So, $\text{res}_0^{\text{r}} = 0$.

PHASE POTENTIAL DIFFERENCE: For the case of CPE, we define $\bar{C}^{\mathrm{r}}_{\mathrm{dl,eff}} = \left(\bar{C}_{\mathrm{dl}}\right)^{2-n^{\mathrm{r}}_{\mathrm{dl}}} (\omega_{\mathrm{dl}})^{n^{\mathrm{r}}_{\mathrm{dl}}-1}$. Then, the LF behavior of $\widetilde{\Phi}^{\mathrm{r}}_{\mathrm{s\text{-}e}}(\tilde{x}, s)/I_{\mathrm{app}}(s)$ has integration dynamics for which then negative- and positive-electrode residues are:

$$\mathrm{res}^{\mathrm{n}}_0 = \frac{\left|\theta^{\mathrm{p}}_{100} - \theta^{\mathrm{p}}_0\right| \, [U^{\mathrm{n}}_{\mathrm{ocp}}]'}{\bar{C}^{\mathrm{n}}_{\mathrm{dl,eff}} \left|\theta^{\mathrm{p}}_{100} - \theta^{\mathrm{p}}_0\right| \, [U^{\mathrm{n}}_{\mathrm{ocp}}]' - 3600Q}$$

$$\mathrm{res}^{\mathrm{p}}_0 = \frac{-\left|\theta^{\mathrm{p}}_{100} - \theta^{\mathrm{p}}_0\right| \, [U^{\mathrm{p}}_{\mathrm{ocp}}]'}{\bar{C}^{\mathrm{p}}_{\mathrm{dl,eff}} \left|\theta^{\mathrm{p}}_{100} - \theta^{\mathrm{p}}_0\right| \, [U^{\mathrm{p}}_{\mathrm{ocp}}]' - 3600Q}.$$

The corresponding integrator-removed TFs are:

$$\frac{[\widetilde{\Phi}^{\mathrm{r}}_{\mathrm{s\text{-}e}}(\tilde{x}, s)]^*}{I_{\mathrm{app}}(s)} = \frac{\widetilde{\Phi}^{\mathrm{r}}_{\mathrm{s\text{-}e}}(\tilde{x}, s)}{I_{\mathrm{app}}(s)} - \frac{\mathrm{res}^{\mathrm{r}}_0}{s}.$$

INTERFACIAL LITHIUM FLUX: No integrators in $I^{\mathrm{r}}_{\mathrm{f+dl}}(\tilde{x}, s)/I_{\mathrm{app}}(s)$: $\mathrm{res}^{\mathrm{r}}_0 = 0$.

INTERFACIAL FARADAIC LITHIUM FLUX: $I^{\mathrm{r}}_{\mathrm{f}}(\tilde{x}, s)/I_{\mathrm{app}}(s)$ has no integrators. So, $\mathrm{res}^{\mathrm{r}}_0 = 0$.

INTERFACIAL NONFARADAIC LITHIUM FLUX: $I^{\mathrm{r}}_{\mathrm{dl}}(\tilde{x}, s)/I_{\mathrm{app}}(s)$ has no integrators. So, $\mathrm{res}^{\mathrm{r}}_0 = 0$.

Low-frequency gains

ELECTROLYTE CONCENTRATION: The $\widetilde{\Theta}^{\mathrm{r}}_{\mathrm{e}}(\tilde{x}, s)/I_{\mathrm{app}}(s)$ LF gains are:

$$\frac{\widetilde{\Theta}^{\mathrm{n}}_{\mathrm{e}}(\tilde{x}, 0)}{I_{\mathrm{app}}(0)} = \frac{\bar{q}^{\mathrm{n}}_{\mathrm{e}}\bar{\kappa}^{\mathrm{s}}\bar{\kappa}^{\mathrm{p}} + 3\bar{q}^{\mathrm{s}}_{\mathrm{e}}(\bar{\kappa}^{\mathrm{s}}\bar{\kappa}^{\mathrm{p}} + \bar{\kappa}^{\mathrm{n}}\bar{\kappa}^{\mathrm{p}}) + \bar{q}^{\mathrm{p}}_{\mathrm{e}}(2\bar{\kappa}^{\mathrm{n}}\bar{\kappa}^{\mathrm{s}} + 3\bar{\kappa}^{\mathrm{s}}\bar{\kappa}^{\mathrm{p}} + 6\bar{\kappa}^{\mathrm{n}}\bar{\kappa}^{\mathrm{p}})}{6\bar{\kappa}^{\mathrm{n}}\bar{\kappa}^{\mathrm{s}}\bar{\kappa}^{\mathrm{p}}\bar{\psi}(\bar{q}^{\mathrm{n}}_{\mathrm{e}} + \bar{q}^{\mathrm{s}}_{\mathrm{e}} + \bar{q}^{\mathrm{p}}_{\mathrm{e}})} - \frac{\tilde{x}^2}{2\bar{\kappa}^{\mathrm{n}}\bar{\psi}}$$

$$\frac{\widetilde{\Theta}^{\mathrm{s}}_{\mathrm{e}}(\tilde{x}, 0)}{I_{\mathrm{app}}(0)} = \frac{-2\bar{q}^{\mathrm{n}}_{\mathrm{e}}\bar{\kappa}^{\mathrm{s}}\bar{\kappa}^{\mathrm{p}} + 3\bar{q}^{\mathrm{s}}_{\mathrm{e}}\bar{\kappa}^{\mathrm{n}}\bar{\kappa}^{\mathrm{p}} + 2\bar{q}^{\mathrm{p}}_{\mathrm{e}}(\bar{\kappa}^{\mathrm{n}}\bar{\kappa}^{\mathrm{s}} + 3\bar{\kappa}^{\mathrm{n}}\bar{\kappa}^{\mathrm{p}})}{6\bar{\kappa}^{\mathrm{n}}\bar{\kappa}^{\mathrm{s}}\bar{\kappa}^{\mathrm{p}}\bar{\psi}(\bar{q}^{\mathrm{n}}_{\mathrm{e}} + \bar{q}^{\mathrm{s}}_{\mathrm{e}} + \bar{q}^{\mathrm{p}}_{\mathrm{e}})} - \frac{\tilde{x} - 1}{\bar{\kappa}^{\mathrm{s}}\bar{\psi}}$$

$$\frac{\widetilde{\Theta}_{\rm e}^{\rm p}(\tilde{x},0)}{I_{\rm app}(0)} = \frac{-\bar{q}_{\rm e}^{\rm n}(2\bar{\kappa}^{\rm s}\bar{\kappa}^{\rm p}+3\bar{\kappa}^{\rm n}\bar{\kappa}^{\rm s}+6\bar{\kappa}^{\rm n}\bar{\kappa}^{\rm p})-3\bar{q}_{\rm e}^{\rm s}(\bar{\kappa}^{\rm n}\bar{\kappa}^{\rm s}+\bar{\kappa}^{\rm n}\bar{\kappa}^{\rm p})-\bar{q}_{\rm e}^{\rm p}\bar{\kappa}^{\rm n}\bar{\kappa}^{\rm s}}{6\bar{\kappa}^{\rm n}\bar{\kappa}^{\rm s}\bar{\kappa}^{\rm p}\bar{\psi}(\bar{q}_{\rm e}^{\rm n}+\bar{q}_{\rm e}^{\rm s}+\bar{q}_{\rm e}^{\rm p})} + \frac{(3-\tilde{x})^2}{2\bar{\kappa}^{\rm p}\bar{\psi}}.$$

SOLID SURFACE CONCENTRATION: The LF gain of $\widetilde{\Theta}_{\rm ss}^{\rm r}(\tilde{x},s)/I_{\rm app}(s)$ is infinite. The LF gain of integrator-removed $[\widetilde{\Theta}_{\rm ss}^{\rm r}(\tilde{x},s)]^*/I_{\rm app}(s)$ is:

$$\frac{[\widetilde{\Theta}_{\rm ss}^{\rm r}(\tilde{x},0)]^*}{I_{\rm app}(0)} = z_0^{\rm r} - {\rm res}_0^{\rm r}\bar{\psi}\bar{\kappa}^{\rm r}\frac{[\widetilde{\Theta}_1^{''}(\tilde{x},0)]^{\rm r}}{I_{\rm app}(0)} + 3600{\rm res}_0^{\rm r}\bar{q}_{\rm e}^{\rm r}\frac{\widetilde{\Theta}_{\rm e}^{\rm r}(\tilde{x},0)}{I_{\rm app}(0)},$$

where $\widetilde{\Theta}_{\rm e}^{\rm r}(\tilde{x},0)/I_{\rm app}(0)$ are the LF gains of $\theta_{\rm e}$, from above,

$$z_0^{\rm r} = \frac{\left|\theta_{100}^{\rm r}-\theta_0^{\rm r}\right|\bar{C}_{\rm dl,eff}^{\rm r}\left(\left|\theta_{100}^{\rm r}-\theta_0^{\rm r}\right|[U_{\rm ocp}^{\rm r}]'\bar{R}_{\rm dl}^{\rm r}\bar{C}_{\rm dl,eff}^{\rm r}+3600Q\bar{R}_{\rm ct}^{\rm r}\right)}{\left(\bar{C}_{\rm dl,eff}^{\rm r}\left|\theta_{100}^{\rm r}-\theta_0^{\rm r}\right|[U_{\rm ocp}^{\rm r}]'-3600Q\right)^2} + \frac{(1-n_{\rm dl}^{\rm r})\bar{C}_{\rm dl,eff}^{\rm r}\left|\theta_{100}^{\rm r}-\theta_0^{\rm r}\right|^2[U_{\rm ocp}^{\rm r}]'\left(\bar{C}_{\rm dl}^{\rm r}/\omega_{\rm dl}^{\rm r}\right)}{\left(\bar{C}_{\rm dl,eff}^{\rm r}\left|\theta_{100}^{\rm r}-\theta_0^{\rm r}\right|[U_{\rm ocp}^{\rm r}]'-3600Q\right)^2}.$$

and $[\widetilde{\Theta}_1^{''}(\tilde{x},0)]^{\rm r}/I_{\rm app}(0)$ are coefficients multiplying s in Taylor-series expansion of second spatial derivative of $\theta_{\rm e}$ TF, which are (written in terms of z):

$$[\widetilde{\Theta}_1^{''}(z)]^{\rm n} = \frac{3600\times{\rm num}^{\rm n}}{18\bar{D}_{\rm s}^{\rm n}[U_{\rm ocp}^{\rm n}]'(\bar{q}_{\rm e}^{\rm n}+\bar{q}_{\rm e}^{\rm s}+\bar{q}_{\rm e}^{\rm p})(\bar{\kappa}^{\rm n})^2\bar{\kappa}^{\rm s}\bar{\kappa}^{\rm p}\bar{\sigma}^{\rm n}\bar{\psi}^2}$$

$${\rm num}^{\rm n} = -\Big[-3\bar{D}_{\rm s}^{\rm n}[U_{\rm ocp}^{\rm n}]'\bar{q}_{\rm e}^{\rm n}\Big(\bar{q}_{\rm e}^{\rm n}(1-3z^2)\bar{\kappa}^{\rm s}\bar{\kappa}^{\rm p} + 2\bar{q}_{\rm e}^{\rm p}\bar{\kappa}^{\rm n}\bar{\kappa}^{\rm s}+3\bar{q}_{\rm e}^{\rm s}\bar{\kappa}^{\rm p}(\bar{\kappa}^{\rm n}+\bar{\kappa}^{\rm s}-z^2\bar{\kappa}^{\rm s}) + 3\bar{q}_{\rm e}^{\rm p}\bar{\kappa}^{\rm p}(2\bar{\kappa}^{\rm n}+\bar{\kappa}^{\rm s}-z^2\bar{\kappa}^{\rm s})\Big)\bar{\sigma}^{\rm n}$$

$$+ 3Q\bar{D}_{\rm s}^{\rm n}\left(\left|\theta_{100}^{\rm n}-\theta_0^{\rm n}\right|\right)^{-1}(\bar{q}_{\rm e}^{\rm n}+\bar{q}_{\rm e}^{\rm s}+\bar{q}_{\rm e}^{\rm p})\bar{\kappa}^{\rm s}\bar{\kappa}^{\rm p}\Bigg(T(3z^2-1)\bar{\kappa}_D\bar{\sigma}^{\rm n}$$

$$+ \bar{\psi}((-2+6z-3z^2)\bar{\kappa}^{\rm n}+\bar{\sigma}^{\rm n}-3z^2\bar{\sigma}^{\rm n})\Bigg)\Bigg]$$

$$[\widetilde{\Theta}_1''(z)]^{\rm p} = \frac{3600\times{\rm num}^{\rm p}}{18\bar{D}_{\rm s}^{\rm p}\,[U_{\rm ocp}^{\rm p}]'(\bar{q}_{\rm e}^{\rm n}+\bar{q}_{\rm e}^{\rm s}+\bar{q}_{\rm e}^{\rm p})\bar{\kappa}^{\rm n}\bar{\kappa}^{\rm s}\,(\bar{\kappa}^{\rm p})^2\,\bar{\sigma}^{\rm p}\bar{\psi}^2}$$

$${\rm num}^{\rm p} = \Bigg[-3\bar{D}_{\rm s}^{\rm p}\,[U_{\rm ocp}^{\rm p}]'\bar{q}_{\rm e}^{\rm p}\Bigg(\bar{q}_{\rm e}^{\rm p}(1-3z^2)\bar{\kappa}^{\rm n}\bar{\kappa}^{\rm s}$$

$$+ 2\bar{q}_{\rm e}^{\rm n}\bar{\kappa}^{\rm s}\bar{\kappa}^{\rm p}+3\bar{q}_{\rm e}^{\rm s}\bar{\kappa}^{\rm n}(\bar{\kappa}^{\rm p}+\bar{\kappa}^{\rm s}-z^2\bar{\kappa}^{\rm s})$$

$$+ 3\bar{q}_{\rm e}^{\rm n}\bar{\kappa}^{\rm n}(2\bar{\kappa}^{\rm p}+\bar{\kappa}^{\rm s}-z^2\bar{\kappa}^{\rm s})\Bigg)\bar{\sigma}^{\rm p}$$

$$+ 3Q\bar{D}_{\rm s}^{\rm p}\left(\left|\theta_{100}^{\rm p}-\theta_0^{\rm p}\right|\right)^{-1}(\bar{q}_{\rm e}^{\rm n}+\bar{q}_{\rm e}^{\rm s}+\bar{q}_{\rm e}^{\rm p})\bar{\kappa}^{\rm n}\bar{\kappa}^{\rm s}\Bigg(T(3z^2-1)\bar{\kappa}_D\bar{\sigma}^{\rm p}$$

$$+ \bar{\psi}((-2+6z-3z^2)\bar{\kappa}^{\rm p}+\bar{\sigma}^{\rm p}-3z^2\bar{\sigma}^{\rm p})\Bigg)\Bigg].$$

ELECTROLYTE POTENTIAL: The $\widetilde{\Phi}_{\rm e}^{\rm r}(\tilde{x},s)/I_{\rm app}(s)$ LF gains are:

$$\frac{\widetilde{\Phi}_{\rm e}^{\rm n}(\tilde{x},0)}{I_{\rm app}(0)} = -\frac{\tilde{x}^2}{2\bar{\kappa}^{\rm n}}+\frac{\bar{\kappa}_D T\tilde{x}^2}{2\bar{\psi}\bar{\kappa}^{\rm n}}$$

$$\frac{\widetilde{\Phi}_{\rm e}^{\rm s}(\tilde{x},0)}{I_{\rm app}(0)} = \frac{\widetilde{\Phi}_{\rm e}^{\rm n}(1,0)}{I_{\rm app}(0)}-\frac{\tilde{x}-1}{\bar{\kappa}^{\rm s}}+\frac{\bar{\kappa}_D T(\tilde{x}-1)}{\bar{\psi}\bar{\kappa}^{\rm s}}$$

$$\frac{\widetilde{\Phi}_{\rm e}^{\rm p}(\tilde{x},0)}{I_{\rm app}(0)} = \frac{\widetilde{\Phi}_{\rm e}^{\rm s}(2,0)}{I_{\rm app}(0)}+\frac{(3-\tilde{x})^2-1}{2\bar{\kappa}^{\rm p}}-\frac{\bar{\kappa}_D T\left((3-\tilde{x})^2-1\right)}{2\bar{\psi}\bar{\kappa}^{\rm p}}.$$

SOLID POTENTIAL: The $\widetilde{\Phi}_{\rm s}^{\rm r}(\tilde{x},s)/I_{\rm app}(s)$ LF gains are:

$$\frac{\widetilde{\Phi}_{\rm s}^{\rm n}(\tilde{x},0)}{I_{\rm app}(0)} = \frac{\tilde{x}(\tilde{x}-2)}{2\bar{\sigma}^{\rm n}} \quad \text{and} \quad \frac{\widetilde{\Phi}_{\rm s}^{\rm p}(\tilde{x},0)}{I_{\rm app}(0)} = \frac{-(3-\tilde{x})(1-\tilde{x})}{2\bar{\sigma}^{\rm p}}.$$

PHASE POTENTIAL DIFFERENCE: The LF gain of $\widetilde{\Phi}^{\mathrm{r}}_{\mathrm{s\text{-}e}}(\tilde{x},s)/I_{\mathrm{app}}(s)$ is infinite. The LF gain of integrator-removed $[\widetilde{\Phi}^{\mathrm{r}}_{\mathrm{s\text{-}e}}(\tilde{x},s)]^{*}/I_{\mathrm{app}}(s)$ is:

$$\frac{[\widetilde{\Phi}^{\mathrm{r}}_{\mathrm{s\text{-}e}}(\tilde{x},0)]^{*}}{I_{\mathrm{app}}(0)} = z^{\mathrm{r}}_{0} - \mathrm{res}^{\mathrm{r}}_{0}\bar{\psi}\bar{\kappa}^{\mathrm{r}}\frac{[\widetilde{\Theta}^{''}_{1}(\tilde{x},0)]^{\mathrm{r}}}{I_{\mathrm{app}}(0)} + 3600\mathrm{res}^{\mathrm{r}}_{0}\bar{q}^{\mathrm{r}}_{\mathrm{e}}\frac{\widetilde{\Theta}^{\mathrm{r}}_{\mathrm{e}}(\tilde{x},0)}{I_{\mathrm{app}}(0)},$$

where the $\widetilde{\Theta}^{\mathrm{r}}_{\mathrm{e}}(\tilde{x},0)/I_{\mathrm{app}}(0)$ and $[\widetilde{\Theta}^{''}_{1}(\tilde{x},0)]^{\mathrm{r}}/I_{\mathrm{app}}(0)$ terms are the same as above, but where we now have:

$$\begin{aligned}
z^{\mathrm{r}}_{0} &= \lim_{s\to 0}\bar{Z}^{\mathrm{r}}_{\tilde{\mathrm{s}}\tilde{\mathrm{e}}}(s) - \frac{\mathrm{res}^{\mathrm{r}}_{0}}{s} \\
&= \frac{\left(\bar{C}^{\mathrm{r}}_{\mathrm{dl,eff}}\left|\theta^{\mathrm{r}}_{100}-\theta^{\mathrm{r}}_{0}\right|\,[U^{\mathrm{r}}_{\mathrm{ocp}}]'\right)^{2}\bar{R}^{\mathrm{r}}_{\mathrm{dl}} + (3600Q)^{2}\,\bar{R}^{\mathrm{r}}_{\mathrm{ct}}}{\left(\bar{C}^{\mathrm{r}}_{\mathrm{dl,eff}}\left|\theta^{\mathrm{r}}_{100}-\theta^{\mathrm{r}}_{0}\right|\,[U^{\mathrm{r}}_{\mathrm{ocp}}]' - 3600Q\right)^{2}} \\
&\quad - \frac{3600Q\left|\theta^{\mathrm{r}}_{100}-\theta^{\mathrm{r}}_{0}\right|\,[U^{\mathrm{r}}_{\mathrm{ocp}}]'}{15\bar{D}^{\mathrm{r}}_{\mathrm{s}}\left(\bar{C}^{\mathrm{r}}_{\mathrm{dl,eff}}\left|\theta^{\mathrm{r}}_{100}-\theta^{\mathrm{r}}_{0}\right|\,[U^{\mathrm{r}}_{\mathrm{ocp}}]' - 3600Q\right)^{2}} \\
&\quad - \frac{(1-n^{\mathrm{r}}_{\mathrm{dl}})\left(\bar{C}^{\mathrm{r}}_{\mathrm{dl}}/\omega^{\mathrm{r}}_{\mathrm{dl}}\right)\bar{C}^{\mathrm{r}}_{\mathrm{dl,eff}}\left(\left|\theta^{\mathrm{r}}_{100}-\theta^{\mathrm{r}}_{0}\right|\,[U^{\mathrm{r}}_{\mathrm{ocp}}]'\right)^{2}}{\left(\bar{C}^{\mathrm{r}}_{\mathrm{dl,eff}}\left|\theta^{\mathrm{r}}_{100}-\theta^{\mathrm{r}}_{0}\right|\,[U^{\mathrm{r}}_{\mathrm{ocp}}]' - 3600Q\right)^{2}} + \bar{R}^{\mathrm{r}}_{\mathrm{f}}
\end{aligned}$$

INTERFACIAL LITHIUM FLUX: The $I^{\mathrm{r}}_{\mathrm{f+dl}}(\tilde{x},s)/I_{\mathrm{app}}(s)$ LF gains are:

$$\frac{I^{\mathrm{n}}_{\mathrm{f+dl}}(\tilde{x},0)}{I_{\mathrm{app}}(0)} = 1 \qquad \text{and} \qquad \frac{I^{\mathrm{p}}_{\mathrm{f+dl}}(\tilde{x},0)}{I_{\mathrm{app}}(0)} = -1.$$

INTERFACIAL FARADAIC LITHIUM FLUX: The $I^{\mathrm{r}}_{\mathrm{f}}(\tilde{x},s)/I_{\mathrm{app}}(s)$ LF gains are:

$$\frac{I^{\mathrm{r}}_{\mathrm{f}}(\tilde{x},0)}{I_{\mathrm{app}}(0)} = \frac{3600Q}{3600Q - \bar{C}^{\mathrm{r}}_{\mathrm{dl,eff}}\left|\theta^{\mathrm{r}}_{100}-\theta^{\mathrm{r}}_{0}\right|\,[U^{\mathrm{r}}_{\mathrm{ocp}}]'}\frac{I^{\mathrm{r}}_{\mathrm{f+dl}}(\tilde{x},0)}{I_{\mathrm{app}}(0)}.$$

INTERFACIAL NONFARADAIC LITHIUM FLUX: $I^{\mathrm{r}}_{\mathrm{dl}}(\tilde{x},s)/I_{\mathrm{app}}(s)$ LF gains are:

$$\frac{I^{\mathrm{r}}_{\mathrm{dl}}(\tilde{x},0)}{I_{\mathrm{app}}(0)} = \frac{-\bar{C}^{\mathrm{r}}_{\mathrm{dl,eff}}\left|\theta^{\mathrm{r}}_{100}-\theta^{\mathrm{r}}_{0}\right|\,[U^{\mathrm{r}}_{\mathrm{ocp}}]'}{\left(3600Q - \bar{C}^{\mathrm{r}}_{\mathrm{dl,eff}}\left|\theta^{\mathrm{r}}_{100}-\theta^{\mathrm{r}}_{0}\right|\,[U^{\mathrm{r}}_{\mathrm{ocp}}]'\right)}\frac{I^{\mathrm{r}}_{\mathrm{f+dl}}(\tilde{x},0)}{I_{\mathrm{app}}(0)}.$$

High-frequency gains

- To find HF gains, we notice that old and new TFs have identical HF limits and define (cf. App. 2.d):

$$\nu^{\mathrm{r}}_{\infty} = \lim_{s\to\infty} \nu^{\mathrm{r}}(s) = \sqrt{\frac{1}{\bar{\sigma}^{\mathrm{r}}} + \frac{1}{\bar{\kappa}^{\mathrm{r}}}} \Bigg/ \sqrt{\bar{R}^{\mathrm{r}}_{\mathrm{f}} + \left(\frac{1}{\bar{R}^{\mathrm{r}}_{\mathrm{ct}}} + \frac{1}{\bar{R}^{\mathrm{r}}_{\mathrm{dl}}}\right)^{-1}}.$$

- Then, HF gains of the TFs of interest are listed below.

ELECTROLYTE CONCENTRATION: HF gains of $\widetilde{\Theta}^{\mathrm{r}}_{\mathrm{e}}(\tilde{x}, s)/I_{\mathrm{app}}(s)$ are zero.

SOLID SURFACE CONCENTRATION: HF gains of $\widetilde{\Theta}^{\mathrm{r}}_{\mathrm{ss}}(\tilde{x}, s)/I_{\mathrm{app}}(s)$ are zero.

ELECTROLYTE POTENTIAL: HF gains of $\widetilde{\Phi}^{\mathrm{r}}_{\mathrm{e}}(\tilde{x}, s)/I_{\mathrm{app}}(s)$ are:

$$\frac{\widetilde{\Phi}^{\mathrm{n}}_{\mathrm{e}}(\tilde{x}, \infty)}{I_{\mathrm{app}}(\infty)} = \frac{\cosh(\nu^{\mathrm{n}}_{\infty}) - \cosh(\nu^{\mathrm{n}}_{\infty}(1-\tilde{x}))}{(\bar{\sigma}^{\mathrm{n}} + \bar{\kappa}^{\mathrm{n}})\sinh(\nu^{\mathrm{n}}_{\infty})\nu^{\mathrm{n}}_{\infty}} + \frac{\bar{\sigma}^{\mathrm{n}}\left(1 - \cosh(\nu^{\mathrm{n}}_{\infty}\tilde{x})\right)}{\bar{\kappa}^{\mathrm{n}}(\bar{\sigma}^{\mathrm{n}} + \bar{\kappa}^{\mathrm{n}})\sinh(\nu^{\mathrm{n}}_{\infty})\nu^{\mathrm{n}}_{\infty}} - \frac{\tilde{x}}{\bar{\sigma}^{\mathrm{n}} + \bar{\kappa}^{\mathrm{n}}}$$

$$\frac{\widetilde{\Phi}^{\mathrm{s}}_{\mathrm{e}}(\tilde{x}, \infty)}{I_{\mathrm{app}}(\infty)} = \frac{\widetilde{\Phi}^{\mathrm{n}}_{\mathrm{e}}(1, \infty)}{I_{\mathrm{app}}(\infty)} - \frac{\tilde{x} - 1}{\bar{\kappa}^{\mathrm{s}}}$$

$$\frac{\widetilde{\Phi}^{\mathrm{p}}_{\mathrm{e}}(\tilde{x}, \infty)}{I_{\mathrm{app}}(\infty)} = \frac{\widetilde{\Phi}^{\mathrm{s}}_{\mathrm{e}}(2, \infty)}{I_{\mathrm{app}}(\infty)} - \frac{1 - \cosh(\nu^{\mathrm{p}}_{\infty}(\tilde{x}-2))}{(\bar{\sigma}^{\mathrm{p}} + \bar{\kappa}^{\mathrm{p}})\sinh(\nu^{\mathrm{p}}_{\infty})\nu^{\mathrm{p}}_{\infty}} - \frac{\bar{\sigma}^{\mathrm{p}}\left(\cosh(\nu^{\mathrm{p}}_{\infty}) - \cosh(\nu^{\mathrm{p}}_{\infty}(3-\tilde{x}))\right)}{\bar{\kappa}^{\mathrm{p}}(\bar{\sigma}^{\mathrm{p}} + \bar{\kappa}^{\mathrm{p}})\sinh(\nu^{\mathrm{p}}_{\infty})\nu^{\mathrm{p}}_{\infty}} - \frac{\tilde{x} - 2}{\bar{\sigma}^{\mathrm{p}} + \bar{\kappa}^{\mathrm{p}}}.$$

SOLID POTENTIAL: HF gains of $\widetilde{\Phi}^{\mathrm{r}}_{\mathrm{s}}(\tilde{x}, s)/I_{\mathrm{app}}(s)$ are:

$$\frac{\widetilde{\Phi}^{\mathrm{n}}_{\mathrm{s}}(\tilde{x}, \infty)}{I_{\mathrm{app}}(\infty)} = \frac{-\bar{\kappa}^{\mathrm{n}}\left(\cosh(\nu^{\mathrm{n}}_{\infty}) - \cosh(\nu^{\mathrm{n}}_{\infty}(\tilde{x}-1))\right) - \bar{\sigma}^{\mathrm{n}}\left(1 - \cosh(\nu^{\mathrm{n}}_{\infty}\tilde{x})\right)}{\bar{\sigma}^{\mathrm{n}}(\bar{\kappa}^{\mathrm{n}} + \bar{\sigma}^{\mathrm{n}})\sinh(\nu^{\mathrm{n}}_{\infty})\nu^{\mathrm{n}}_{\infty}} - \frac{\tilde{x}}{\bar{\kappa}^{\mathrm{n}} + \bar{\sigma}^{\mathrm{n}}}$$

$$\frac{\widetilde{\Phi}_{\rm s}^{\rm p}(\tilde{x},\infty)}{I_{\rm app}(\infty)} = \frac{\bar{\kappa}^{\rm p}\left(\cosh(\nu_\infty^{\rm p})-\cosh(\nu_\infty^{\rm p}(2-\tilde{x}))\right)+\bar{\sigma}^{\rm p}\left(1-\cosh(\nu_\infty^{\rm p}(3-\tilde{x}))\right)}{\bar{\sigma}^{\rm p}\left(\bar{\kappa}^{\rm p}+\bar{\sigma}^{\rm p}\right)\sinh(\nu_\infty^{\rm p})\nu_\infty^{\rm p}} + \frac{3-\tilde{x}}{\bar{\kappa}^{\rm p}+\bar{\sigma}^{\rm p}}.$$

PHASE POTENTIAL DIFFERENCE: HF gains of both $\widetilde{\Phi}_{\rm s\text{-}e}^{\rm r}(\tilde{x},s)/I_{\rm app}(s)$ and $[\widetilde{\Phi}_{\rm s\text{-}e}^{\rm r}(\tilde{x},s)]^*/I_{\rm app}(s)$ are (even when $n_{\rm sf}\neq 1$):

$$\frac{\widetilde{\Phi}_{\rm s\text{-}e}^{\rm n}(\tilde{x},\infty)}{I_{\rm app}(\infty)} = \frac{\bar{\sigma}^{\rm n}\cosh(\nu_\infty^{\rm n}\tilde{x})+\bar{\kappa}^{\rm n}\cosh(\nu_\infty^{\rm n}(\tilde{x}-1))}{\bar{\sigma}^{\rm n}\bar{\kappa}^{\rm n}\sinh(\nu_\infty^{\rm n})\nu_\infty^{\rm n}}$$

$$\frac{\widetilde{\Phi}_{\rm s\text{-}e}^{\rm p}(\tilde{x},\infty)}{I_{\rm app}(\infty)} = \frac{-\bar{\sigma}^{\rm p}\cosh(\nu_\infty^{\rm p}(3-\tilde{x}))-\bar{\kappa}^{\rm p}\cosh(\nu_\infty^{\rm p}(2-\tilde{x}))}{\bar{\sigma}^{\rm p}\bar{\kappa}^{\rm p}\sinh(\nu_\infty^{\rm p})\nu_\infty^{\rm p}}.$$

INTERFACIAL LITHIUM FLUX: HF gains of $I_{\rm f+dl}^{\rm r}(\tilde{x},s)/I_{\rm app}(s)$ are:

$$\frac{I_{\rm f+dl}^{\rm n}(\tilde{x},\infty)}{I_{\rm app}(\infty)} = \frac{\nu_\infty^{\rm n}\left[\bar{\sigma}^{\rm n}\cosh(\nu_\infty^{\rm n}\tilde{x})+\bar{\kappa}^{\rm n}\cosh(\nu_\infty^{\rm n}(\tilde{x}-1))\right]}{(\bar{\kappa}^{\rm n}+\bar{\sigma}^{\rm n})\sinh(\nu_\infty^{\rm n})}$$

$$\frac{I_{\rm f+dl}^{\rm p}(\tilde{x},\infty)}{I_{\rm app}(\infty)} = -\frac{\nu_\infty^{\rm p}\left[\bar{\sigma}^{\rm p}\cosh(\nu_\infty^{\rm p}(3-\tilde{x}))+\bar{\kappa}^{\rm p}\cosh(\nu_\infty^{\rm p}(2-\tilde{x}))\right]}{(\bar{\kappa}^{\rm p}+\bar{\sigma}^{\rm p})\sinh(\nu_\infty^{\rm p})}.$$

INTERFACIAL FARADAIC LITHIUM FLUX: HF gains of $I_{\rm f}^{\rm r}(\tilde{x},s)/I_{\rm app}(s)$ are:

$$\frac{I_{\rm f}^{\rm r}(\tilde{x},\infty)}{I_{\rm app}(\infty)} = \frac{\bar{R}_{\rm dl}^{\rm r}}{\bar{R}_{\rm ct}^{\rm r}+\bar{R}_{\rm dl}^{\rm r}}\frac{I_{\rm f+dl}^{\rm r}(\tilde{x},\infty)}{I_{\rm app}(\infty)}.$$

INTERFACIAL NONFARADAIC LITHIUM FLUX: HF gains of $I_{\rm dl}^{\rm r}(\tilde{x},s)/I_{\rm app}(s)$:

$$\frac{I_{\rm dl}^{\rm r}(\tilde{x},\infty)}{I_{\rm app}(\infty)} = \frac{\bar{R}_{\rm ct}^{\rm r}}{\bar{R}_{\rm dl}^{\rm r}+\bar{R}_{\rm ct}^{\rm r}}\frac{I_{\rm f+dl}^{\rm r}(\tilde{x},\infty)}{I_{\rm app}(\infty)}.$$

Appendix 2.f: "NMC30 cell" parameters used in examples

- Parameter values for the "NMC30 cell" used in examples are tabulated here.
- MSMR-model values are tabulated to right.

Graphite			NMC111		
U_j^0 [V]	X_j	ω_j	U_j^0 [V]	X_j	ω_j
0.0887	0.1672	0.0631	3.7467	0.3559	1.8350
0.0913	0.2076	0.0140	3.9215	0.0330	1.3443
0.1305	0.1979	0.0314	4.0459	0.0734	2.6936
0.1330	0.3157	1.1177	4.4178	0.3711	8.2197
0.2164	0.0591	0.0728	7.0845	0.1666	3.3176
0.3673	0.0395	3.2005			
1.2093	0.0130	10.7190			

- Cell parameters in standard format are:

Symbol	Units	Negative electrode	Separator	Positive electrode
L	μm	46.6	18.7	43
R	μm	6.3	—	2.13
σ	S m^{-1}	1000	—	10
ε_s	m^{3}m^{-3}	0.4925	—	0.5724
ε_e	m^{3}m^{-3}	0.292	0.3949	0.209
brug	—	1.52	1.62	1.44
$c_{s,max}$	mol m^{-3}	31 390	—	48 390
θ_0	—	0.014	—	0.9615
θ_{100}	—	0.884	—	0.4352
$D_{s,ref}$	m^2 s^{-1}	2.6463×10^{-14}	—	7.6885×10^{-16}
k_{norm}	mol m^2 s^{-1}	1.5401×10^{-4}	—	1.0426×10^{-4}
α	—	0.5	—	0.5
R_{dl}	Ω m^2	1.9426×10^{-4}	—	6.162×10^{-5}
C_{dl}	F m^{-2}	1.47	—	0.198
R_f	Ω m^2	9.713×10^{-4}	—	6.162×10^{-4}
A	m^2		1.7775	
$c_{e,0}$	mol m^{-3}		1000	
D_e	m^2 s^{-1}		2.7945×10^{-10}	
t_+^0	—		0.26	
R_c	mΩ		0.534	
$\mathrm{d}\ln f_\pm/\mathrm{d}\ln c_e$	—		0	

We compute $\sigma_{eff} = \sigma\varepsilon_s^{brug}$, $\kappa_{eff} = \kappa\varepsilon_e^{brug}$, $D_{e,eff} = D_e\varepsilon_e^{brug}$. In the electrolyte, κ is a function of c_e:

$$\kappa(c_e) = c_e(0.0420 - 1.0972\times10^{-5}c_e + 0.0132\exp(-0.0022c_e))^2.$$

OCP functions are evaluated using the MSMR parameters; $n_f^r = n_{dl}^r = 1$; $\omega_{dl}^r = 2\pi\times10^{-5}$.

- Cell parameters in lumped format are:

Symbol	Units	Negative electrode	Separator	Positive electrode
$\bar{\sigma}$	S	1.3×10^{7}	—	185109
$\bar{\kappa}$	S	6199	22274	4580
θ_0	—	0.014	—	0.9615
θ_{100}	—	0.884	—	0.4352
$\bar{D}_{\mathrm{s,ref}}$	s^{-1}	6.6674×10^{-4}	—	1.695×10^{-4}
$\bar{q}_{\mathrm{e}}$	Ah	0.876	0.4754	0.5786
$\bar{k}_0$	A	288.67	—	619.9
α	—	0.5	—	0.5
$\bar{R}_{\mathrm{dl}}$	Ω	1×10^{-5}	—	1×10^{-6}
$\bar{C}_{\mathrm{dl}}$	F	28.556	—	12.2
$\bar{R}_{\mathrm{f}}$	Ω	5×10^{-5}	—	1×10^{-5}
Q	Ah		29.86	
$\bar{\psi}$	V		0.0345158	
$\bar{\kappa}_D$	$\mathrm{V\,K}^{-1}$		-1.275×10^{-4}	
R_{c}	mΩ		0.534	
OCP functions are evaluated using the MSMR parameters; $n_{\mathrm{f}}^{\mathrm{r}} = n_{\mathrm{dl}}^{\mathrm{r}} = 1$; $\omega_{\mathrm{dl}}^{\mathrm{r}} = 2\pi \times 10^{-5}$.				