

Process for lumping parameters to enable nondestructive parameter estimation for lithium-ion physics-based models

Gregory L. Plett^{1,2}, M. Scott Trimboli^{1,3}

¹*Department of Electrical and Computer Engineering, University of Colorado Colorado Springs,*
Colorado Springs, CO 80918, United States, ²*gplett@uccs.edu,* ³*mtrimbol@uccs.edu*

Summary

The classical physics-based Doyle–Fuller–Newman (DFN) lithium-ion cell model is non-identifiable; i.e., it is mathematically impossible to determine the model’s parameter values without ambiguity from nondestructive input/output (current/voltage) measurements. This paper presents a method for converting the DFN model into a “lumped-parameter model” (LPM) that is identifiable: i.e., it is mathematically possible to determine its parameter values from input/output measurements. This is a requirement for being able to estimate the parameters of a physics-based model of a specific lithium-ion cell using non-destructive methods, and is an important step in making BMS using physics-based models feasible.

1 Abstract

Most modern BMS use equivalent-circuit models (ECMs) with algorithms that estimate state of charge, state of health, etc. (SOx). However, ECMs are able to predict only the current/voltage behaviors of a cell and cannot predict its internal electrochemical variables. Since it is exactly these internal variables that give information regarding when we might expect the onset of premature aging, we prefer instead to use physics-based models (PBMs), which can predict these internal variables and so can be used by BMS to compute controls that maximize a tradeoff between performance, service life, and safety.

A drawback to using PBMs is that they have many parameter values that must be estimated to model a specific cell. For example, the standard Doyle–Fuller–Newman (DFN) pseudo-two-dimensional (P2D) model has 36 parameter values (cf. Table 1(left)). However, it turns out to be mathematically impossible to do so using nondestructive tests—tests that rely only on input/output measurements without requiring cell teardown and specialized experimental procedures. This fact is not widely understood and we still see many papers where authors attempt to estimate DFN parameters from nondestructive tests.

A model is said to be non-identifiable if there exist two different sets of model parameter values that give the same input/output function [1]; the DFN model is non-identifiable in this sense. However, in this paper we show a process for grouping or lumping parameters together to make a PBM that is identifiable. The resulting “lumped-parameter model” (LPM) still predicts all cell internal electrochemical variables (or scaled versions thereof), so can be used in advanced BMS based on PBMs.

2 Review of the DFN model

Fig. 1 illustrates the geometry of a 1-d slice through a lithium-ion cell, roughly to typical scale. The cell comprises three main sections: the negative electrode, the separator, and the positive-electrode re-

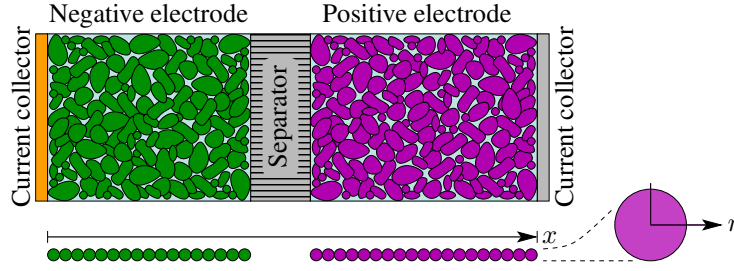


Figure 1: Illustration of the cross-sectional geometry of a lithium-ion cell.

gions. In the diagram, the thickness dimension is denoted by the variable x . The P2D model simplifies electrode-model equations by assuming that all electrode particles are spherical and have identical radius R_s . Then, the radial dimension inside any particle is denoted by the variable r . In the model, the length dimension is physical but the radial dimension is artificial because of this assumption: this is why the model is referred to as a “pseudo” 2-d model. The radial dimension is the pseudo dimension.

The P2D model describes the operation of a lithium-ion cell using four PDEs along with associated boundary conditions and initial values, as well as a single nonlinear algebraic equation that serves as a coupling closure term. This set of equations describes the following physical variables of the cell at spatial location x and time t :

- The concentration of lithium in the solid electrode particles, denoted as $c_s(x, r, t)$ and the concentration in the particles at the particle/electrolyte boundary $c_{s,e}(x, t)$,
- The concentration of lithium in the electrolyte, denoted as $c_e(x, t)$,
- The potential in the solid electrode particles, denoted as $\phi_s(x, t)$,
- The potential in the electrolyte, denoted as $\phi_e(x, t)$, and
- The lithium flux from solid electrode particles into the electrolyte, denoted as $j(x, t)$.

The model equations are summarized in Table 2. We review it here. First, note that all variables are functions of x and t but this dependence will be dropped from the notation unless it is required to clarify some specific point. Further, all parameters are functions of the cell region being described by the equation being reviewed, but their values are assumed to be uniform (constant) across that cell region.

EQUATION I: CHARGE CONSERVATION IN THE SOLID. The first equation we review describes charge conservation within the solid particles that form an electrode. This is modeled by Eq. (5) where σ_{eff}^r is the effective conductivity of the electrode, a_s^r is the specific interfacial surface area of the electrode, and F is Faraday’s constant. The superscript “r”, for “region”, indicates that this equation is parameterized by different constants in different regions of the cell. When it is important to be more specific, we use superscripts “n” for the negative electrode, “s” for the separator, and “p” for the positive electrode. Eq. (5) applies only to the negative-electrode and positive-electrode regions of the cell. It is a linear diffusion equation describing electron movement, with a forcing term that models flux of electrons, which is equal to the flux of lithium from the electrode to the electrolyte locally. The boundary conditions for the PDE are stated in Eqs. (6) and (7), where L^n is the thickness of the negative electrode, L^s is the thickness of the separator, L^p is the thickness of the positive electrode, $L^{\text{tot}} = L^n + L^s + L^p$, A is the surface area of the current collector, and i_{app} is the electrical current measured at the terminals of the cell. (In the sign convention that we use, $i_{\text{app}} > 0$ for discharge currents and $i_{\text{app}} < 0$ for charge currents.) The initial values for this PDE are listed in Eq. (8), where $\theta_s^r = c_s^r / c_{s,\text{max}}^r$ is the stoichiometry of the electrode such that $0 \leq \theta_s^r \leq 1$, $\theta_{s,0}^r = c_{s,0}^r / c_{s,\text{max}}^r$ is the initial equilibrium stoichiometry of the electrode, and $U_{\text{ocp}}^r(\theta_s^r)$ is the open-circuit potential (OCP) of the electrode as a function of local stoichiometry.

EQUATION II: MASS CONSERVATION IN THE SOLID. The second PDE describes mass conservation in the solid electrode materials. It is also valid only for the negative-electrode and positive-electrode regions and is modeled by Eq. (9), where D_s^r is the solid diffusivity of the electrode. This equation is a restatement of Fick’s second law, formulated in spherical coordinates and assuming spherical symmetry. That is, lithium motion inside electrode particles is modeled as standard linear diffusion. The boundary conditions imposed on this PDE are given by Eq. (10), and the initial values are given by Eq. (11), where $0 \leq z_0 \leq 1$ is initial cell state of charge, θ_0^r is the value of θ_s^r when the cell is resting at 0 % SOC, and θ_{100}^r is the value of θ_s^r when the cell is resting at 100 % SOC.

EQUATION III: CHARGE CONSERVATION IN THE ELECTROLYTE. The third PDE describes charge conservation in the electrolyte and is valid for all cell regions. It is modeled using Eq. (12), where κ_{eff}^r is the effective conductivity of the electrolyte, R is the universal gas constant, t_+^0 is the transference number of the positive ion in the electrolyte with respect to the solvent, and f_{\pm} is the mean molar activity coefficient. This equation is dominated by linear-diffusion terms, but the $\partial \ln c_e / \partial x$ term modifies the relationship somewhat to account for a nonlinear concentration dependence. The boundary conditions of Eqs. (13) and (14) enforce the physical constraint that all current at the current-collector boundaries must be electronic and all current at the separator boundaries must be ionic. Initial values across the entire cell are given by Eq. (15).

EQUATION IV: MASS CONSERVATION IN THE ELECTROLYTE. The fourth PDE describes mass conservation in the electrolyte and is valid for all cell regions. It is modeled as Eq. (16) where ε_e^r is the porosity (volume fraction of the electrolyte in the cell region), and $D_{e,\text{eff}}^r$ is the diffusivity of lithium in the electrolyte. This is again a linear diffusion equation with a forcing term that describes the addition of lithium due to flux of lithium from the electrode into the electrolyte locally. It applies to all regions of the cell. The boundary conditions on this PDE are listed in Eqs. (17) to (19) and enforce continuity flux of lithium across regions of the cell, and also enforce that there be no movement of lithium from inside the cell to the exterior of the cell. Continuity of concentration at the electrode/separator boundaries is also assumed. Initial values across the cell are listed in Eq. (20).

EQUATION V: KINETICS. The final model equation is a nonlinear algebraic closure term known as the Butler–Volmer equation. It describes the kinetics of the cell—the rate of reaction and hence the rate of lithium flux from the electrode particles into the electrolyte comprising Eqs. (21) to (23), where α^r is the charge-transfer coefficient, η^r is the local overpotential, j_0^r is the exchange-flux density, $k_{\text{norm},0}^r$ is a reaction-rate constant, and R_f^r is the resistivity of the surface film that may exist on the electrode particles. This equation is valid for the negative- and positive-electrode regions and is a good description of reaction kinetics for constant-current events, but misses some critical cell behaviors at high frequencies. In [2], the procedure presented in this paper is applied to an interface model that also includes an electric double layer, but we omit those details here for clarity.

3 Reducing number of parameters: Method

The governing equations reviewed in Sect. 2 contain 36 parameter values (plus U_{ocp}^r relationships) that must be determined to use the cell model. These are listed in Table 1. If possible, we would like to find ways to estimate the values of these parameters for a specific cell without opening (or “tearing down”) the cell and performing invasive measurements. That is, we would prefer to use only input/output current/voltage measurements to find parameter values.

It turns out that some of the parameters in Table 1 cannot be estimated uniquely from input/output data. We will demonstrate that it is mathematically impossible to do so. Technically, we state that these parameters are *unidentifiable*. However, the governing equations listed in Sect. 2 can be manipulated to combine together the unidentifiable parameters into a smaller group of *lumped parameters* that are possible to estimate from input/output data, at least in principle. The resulting lumped-parameter model (LPM) retains the ability to predict voltage and (scaled) versions of the cell’s internal variables, and can be used in BMS algorithms to optimize a tradeoff between performance and life.

The first lumped-parameter version of the DFN model of which we are aware was published in [3], although the procedure for doing so was not presented. This LPM was refined over time to include the description of an electrical double layer from [4], presented in [2,5]. A version of the model has appeared in other recent work [6]. To the best of our knowledge, however, we are not aware of any publication that presents the methods for converting the non-identifiable DFN model to an identifiable LPM. That is the purpose of this paper.

We will develop the LPM by modifying the standard PBM equation-by-equation; Fig. 2 shows the process. First, we normalize length scales and then we create new pseudo-dimensionless variable. This exposes parameters that always appear in groups, which we lump together. Finally, we recast the model equations using variables having more convenient names. By the end of this paper, we will have reformulated all equations to eliminate redundant parameters, condensing the parameters we must determine from cell tests to characterize the dynamics of a cell to a minimum identifiable set.

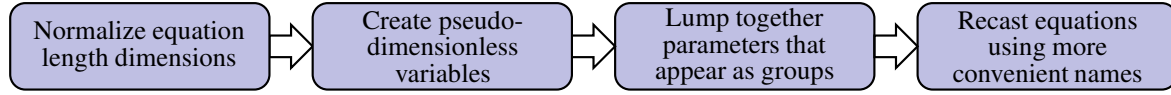


Figure 2: General steps to parameter-lumping process.

3.1 Intensive versus extensive quantities

A quick example might help illustrate the issue we are trying to solve. Consider Ohm’s law, which states: “voltage equals resistance times current”. But, this is equivalent to saying, “voltage equals current divided by the product of conductivity times length”. So, both $V = RI$ and $V = I/(\sigma L)$ are true. Suppose that we measure $V = 1\text{ V}$ and $I = 1\text{ A}$. We can easily calculate $R = V/I = 1\ \Omega$. But, based only on these measured V and I , we have *no idea* what are the distinct values of σ and L .

- We could have $\sigma = 1\text{ S m}^{-1}$ and $L = 1\text{ m}$;
- We could have $\sigma = 0.5\text{ S m}^{-1}$ and $L = 2\text{ m}$;
- We could have $\sigma = 2\text{ S m}^{-1}$ and $L = 0.5\text{ m}$;

and infinitely many other combinations.

The issue is that σ and L are joined together in Ohm’s model in a way that is *impossible* to separate mathematically using measurements of only $\{V, I\}$. It simply cannot be done. We would need to perform an independent *kind* of experiment (e.g., measure σ or L directly) to determine both values with certainty. Why is this a problem with our PBMs? Note that we say that a property is *intensive* if it is a normalized quantity. If everything (dimensions, moles, etc.) in a system is doubled, the value of an intensive property remains unchanged. Examples of intensive properties are pressure, temperature, concentration, and density. Alternately, we say that a property is *extensive* if it is a total quantity. If everything in a system is doubled, the value of an extensive property also doubles. Examples of extensive properties are internal energy, Gibbs free energy, volume, and mass.

Many battery researchers prefer to work with intensive properties. This allows deriving models that apply directly to any scale, whereby we scale intensive values to fit a particular application. But, for the nontear-down parameter-estimation problem, we *require* extensive properties! This is for the same reason that we could compute resistance (extensive) in Ohm’s example but we could not find conductivity (intensive, scaled by length to compute resistance).

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

3.2 How are we going to do this?

Before applying the model-transformation method to the P2D model, we will use it with a simple example to illustrate the process. Assume that we have pairs of measurements (x, y) where $0 \leq x \leq 1$. For simplicity, we skip the step of normalizing x since it already has a normalized range.

Now, suppose that we desire to fit these data to some physically derived relationship:

$$\lambda y = (\alpha \cdot \beta)x + \gamma. \quad (1)$$

We define scaled versions of all of the variables in the equation: we let $\check{y} = y/\bar{y}$ and $\check{x} = x/\bar{x}$. In this notation, an overline ($\bar{\cdot}$) indicates a constant (not yet determined)—usually chosen to normalize the primary variable to make the ($\check{\cdot}$) variable unitless—and ($\check{\cdot}$) is a temporary notation that indicates a (possibly time-varying) variable that has been normalized and (often) made unitless.

When we make this substitution, we write,

$$\begin{aligned} \lambda \bar{y} \check{y} &= (\alpha \cdot \beta) \bar{x} \check{x} + \gamma \\ \check{y} &= \left[\frac{(\alpha \cdot \beta) \bar{x}}{\lambda \bar{y}} \right] \check{x} + \left[\frac{\gamma}{\lambda \bar{y}} \right]. \end{aligned}$$

Now, consider the quantities in brackets. We choose to define $\bar{y} = \gamma/\lambda$ and $\bar{x} = \gamma/(\alpha \cdot \beta)$. Then, we have reformulated the original equation to a simpler form,

$$\check{y} = \check{x} + 1. \quad (2)$$

This equation itself has no more constants that can be estimated.

To implement the physical relationship, we must estimate two values from (x, y) data: a modified slope (reciprocal) \bar{x} and a modified y -intercept \bar{y} . These two parameters (or variations on these) are the only ones that can be estimated from input/output data. In terms of the original relationship of Eq. (1), it is impossible to find unique values for α , β , γ , and λ from input/output data. However, we can implement Eq. (2) and solve for $y = \check{y}\bar{y}$ and for $x = \check{x}\bar{x}$ to find the same variables. We have not lost any ability to predict the variables of the model—we have simply lumped constant parameter values together to make it possible to determine the coefficients of the equation via measured data.

4 Reducing number of parameters: Application

We now apply this method to the PBM PDE model, equation by equation, starting with ϕ_s .

EQUATION 1: CHARGE CONSERVATION IN THE SOLID. The first step to applying the method is to normalize the cell's 1-d thickness dimension by defining:

$$\tilde{x} = (x - x_0^r)/L^r + x_1^r,$$

where x_0^r is the starting location and x_1^r is the index of each region. The result of this normalization is:

$$0 \leq \tilde{x} \leq 1 \text{ in the negative electrode,}$$

$$1 \leq \tilde{x} \leq 2 \text{ in the separator region,}$$

$$2 \leq \tilde{x} \leq 3 \text{ in the positive electrode.}$$

We can also relate derivatives with respect to x to derivatives with respect to \tilde{x} :

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

The second step to applying the method is to define scaled versions of all variables. For the charge-conservation equation, we let $\check{\phi}_s = \phi_s/\bar{\phi}_s$ and $\check{j} = j/\bar{j}$. Note that this also implies that $\partial\phi_s/\partial(\cdot) = \bar{\phi}_s\partial\check{\phi}_s/\partial(\cdot)$. So, starting with Eq. (5) in Table 2, we can write:

$$\begin{aligned} \frac{\partial}{\partial x} \sigma_{\text{eff}}^r \frac{\partial}{\partial x} \phi_s^r &= a_s^r F j^r, \\ \frac{\bar{\phi}_s^r \sigma_{\text{eff}}^r}{(L^r)^2} \frac{\partial^2}{\partial \tilde{x}^2} \check{\phi}_s^r &= a_s^r F \bar{j}^r j^r \\ \frac{\partial^2}{\partial \tilde{x}^2} \check{\phi}_s^r &= F \left[\frac{a_s^r (L^r)^2 \bar{j}^r}{\bar{\phi}_s^r \sigma_{\text{eff}}^r} \right] j^r. \end{aligned}$$

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

Using the same approach, the nonzero boundary conditions of Eq. (6) are rewritten as:

$$\begin{aligned} \frac{\sigma_{\text{eff}}^r \bar{\phi}_s^r}{L^r} \frac{\partial}{\partial \tilde{x}} \check{\phi}_s^r \Big|_{\tilde{x}=0} &= \frac{\sigma_{\text{eff}}^r \bar{\phi}_s^r}{L^r} \frac{\partial}{\partial \tilde{x}} \check{\phi}_s^r \Big|_{\tilde{x}=3} = \frac{-i_{\text{app}}}{A} \\ \left[\frac{A \sigma_{\text{eff}}^r \bar{\phi}_s^r}{L^r} \right] \frac{\partial}{\partial \tilde{x}} \check{\phi}_s^r \Big|_{\tilde{x}=0} &= \left[\frac{A \sigma_{\text{eff}}^r \bar{\phi}_s^r}{L^r} \right] \frac{\partial}{\partial \tilde{x}} \check{\phi}_s^r \Big|_{\tilde{x}=3} = -i_{\text{app}}. \end{aligned}$$

Finally, we consider the initial values from Eq. (8):

- $\phi_{s,0}^n = \check{\phi}_s^n = 0$ in the negative electrode.
- $\phi_{s,0}^p = U_{\text{ocp}}^p(\theta_{s,0}^p) - U_{\text{ocp}}^n(\theta_{s,0}^n)$ in the positive electrode so, $\check{\phi}_{s,0}^p = (U_{\text{ocp}}^p(\theta_{s,0}^p) - U_{\text{ocp}}^n(\theta_{s,0}^n)) / \bar{\phi}_s^p$.

The third step to applying the method is to make assignments to the scaling constants to simplify the equations. We choose to:

- Let $\bar{\phi}_s^r = \frac{L^r}{A \sigma_{\text{eff}}^r}$ and define $\bar{\sigma}^r = \frac{A \sigma_{\text{eff}}^r}{L^r}$, so $\bar{\phi}_s^r = 1/\bar{\sigma}^r$.
- Let $\bar{j}^r = \frac{1}{a_s^r A L^r}$.

This reduces the PDE, its boundary conditions, and initial values to:

$$\begin{aligned}\frac{\partial^2 \check{\phi}_s^r}{\partial \tilde{x}^2} &= F \check{j}^r \\ \frac{\partial}{\partial \tilde{x}} \check{\phi}_s^r \Big|_{\tilde{x}=0} &= \frac{\partial}{\partial \tilde{x}} \check{\phi}_s^r \Big|_{\tilde{x}=3} = -i_{\text{app}} \\ \check{\phi}_{s,0}^n &= 0 \\ \check{\phi}_{s,0}^p &= \left(U_{\text{ocp}}^p(\theta_{s,0}^p) - U_{\text{ocp}}^n(\theta_{s,0}^n) \right) / \bar{\phi}_s^p.\end{aligned}$$

This process has completely eliminated all cell-dependent parameters from the PDE and its boundary conditions, but we still must estimate $\bar{\phi}_s^p$ and specify $\theta_{s,0}^n$ and $\theta_{s,0}^p$ to be able to describe initial values. We must also determine the open-circuit-potential relationships $U_{\text{ocp}}^r(\theta_s^r)$ for both electrodes.

EQUATION II: MASS CONSERVATION IN SOLID. We now apply the same process to the PDE describing mass conservation in the solid, Eq. (9). We normalize the radial pseudo dimension by defining $\tilde{r} = r/R_s^r$; then, $\tilde{r} = 0$ at the center of a particle and $\tilde{r} = 1$ at the surface. We also define $\check{c}_s^r = c_s^r/\bar{c}_s^r$. Substituting these definitions into Eq. (9), we can write:

$$\begin{aligned}\frac{\partial c_s^r}{\partial t} &= \frac{1}{r^2} \frac{\partial}{\partial r} \left(D_s^r r^2 \frac{\partial c_s^r}{\partial r} \right) \\ \bar{c}_s^r \frac{\partial \check{c}_s^r}{\partial t} &= \frac{1}{(R_s^r \tilde{r})^2} \frac{1}{R_s^r} \frac{\partial}{\partial \tilde{r}} \left(D_s^r (R_s^r \tilde{r})^2 \frac{\bar{c}_s^r}{R_s^r} \frac{\partial \check{c}_s^r}{\partial \tilde{r}} \right) \\ \frac{\partial \check{c}_s^r}{\partial t} &= \frac{1}{\tilde{r}^2} \frac{\partial}{\partial \tilde{r}} \left(\left[\frac{D_s^r}{(R_s^r)^2} \right] \tilde{r}^2 \frac{\partial \check{c}_s^r}{\partial \tilde{r}} \right).\end{aligned}$$

The nonzero boundary condition of Eq. (10) is:

$$\begin{aligned}D_s^r \frac{\partial c_s^r}{\partial r} \Big|_{r=R_s^r} &= -j^r \\ \frac{D_s^r \bar{c}_s^r}{R_s^r} \frac{\partial \check{c}_s^r}{\partial \tilde{r}} \Big|_{\tilde{r}=1} &= -\bar{j}^r \check{j}^r \\ \frac{\partial \check{c}_s^r}{\partial \tilde{r}} \Big|_{\tilde{r}=1} &= - \left[\frac{\bar{j}^r R_s^r}{D_s^r \bar{c}_s^r} \right] \check{j}^r.\end{aligned}$$

The initial values of Eq. (11) can be rewritten as:

$$\begin{aligned}c_{s,0}^r &= c_{s,\text{max}}^r (\theta_0^r + z_0(\theta_{100}^r - \theta_0^r)) \\ \check{c}_{s,0}^r &= \bar{c}_{s,\text{max}}^r (\theta_0^r + z_0(\theta_{100}^r - \theta_0^r)).\end{aligned}$$

We now make additional assignments, defining

- $\bar{D}_s^r = \frac{D_s^r}{(R_s^r)^2}$,
- $\bar{c}_s^r = \frac{\bar{j}^r R_s^r}{D_s^r}$ and $\bar{c}_{s,\text{max}}^r = \frac{c_{s,\text{max}}^r}{\bar{c}_s^r} = \frac{a_s^r AL^r c_{s,\text{max}}^r D_s^r}{R_s^r}$.

Note that cell total capacity (in Ah) can be written as¹

$$Q = \varepsilon_s^r AL^r F c_{s,\text{max}}^r |\theta_{100}^r - \theta_0^r| / 3600.$$

If we assume that electrode particles are spherical, then $\varepsilon_s^r = a_s^r R_s^r / 3$. So,

$$\begin{aligned}Q &= \frac{a_s^r AL^r F c_{s,\text{max}}^r R_s^r}{10\,800} |\theta_{100}^r - \theta_0^r| \\ &= \frac{\bar{c}_{s,\text{max}}^r F (R_s^r)^2}{10\,800 D_s^r} |\theta_{100}^r - \theta_0^r|,\end{aligned}$$

or

$$\bar{c}_{s,\text{max}}^r = \frac{10\,800 \bar{D}_s^r Q}{F |\theta_{100}^r - \theta_0^r|}. \quad (3)$$

The benefit of this analysis is that we have replaced two unknown constants, $\bar{c}_{s,\text{max}}^n$ and $\bar{c}_{s,\text{max}}^p$, with a single relationship in terms of a single (easily measurable) cell parameter Q and other constants that must

¹Note that electrochemists may be more comfortable expressing capacity in mol rather than Ah. However, we believe that most engineers will be more familiar with expressing capacity in Ah, and so this will be our convention.

be determined in any case when identifying a model of a lithium-ion cell. We can now express the PDE, its nonzero boundary condition, and its initial values as:

$$\begin{aligned}\frac{\partial \check{c}_s^r}{\partial t} &= \frac{1}{\tilde{r}^2} \frac{\partial}{\partial \tilde{r}} \left(\bar{D}_s^r \tilde{r}^2 \frac{\partial \check{c}_s^r}{\partial \tilde{r}} \right) \\ \frac{\partial \check{c}_s^r}{\partial \tilde{r}} \Big|_{\tilde{r}=1} &= -\check{j}^r \\ \check{c}_{s,0}^r &= \frac{10\,800 \bar{D}_s^r Q}{F |\theta_{100}^r - \theta_0^r|} (\theta_0^r + z_0(\theta_{100}^r - \theta_0^r)).\end{aligned}$$

At this point, the unknown parameters we must estimate are: Q , $\bar{\sigma}^p$, θ_0^n , θ_0^p , θ_{100}^n , θ_{100}^p , \bar{D}_s^n , and \bar{D}_s^p .

EQUATION III: CHARGE CONSERVATION IN THE ELECTROLYTE. We proceed by applying the same methodology to the PDE that describes charge conservation in the electrolyte, Eq. (12). We let $\check{\phi}_e^r = \phi_e^r / \bar{\phi}_e^r$ and $\check{c}_e^r = c_e^r / \bar{c}_e^r$. This gives:

$$\begin{aligned}\frac{\partial}{\partial x} \kappa_{\text{eff}}^r \left(\frac{\partial}{\partial x} \phi_e^r + \frac{2RT(t_+^0 - 1)}{F} \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_e} \right) \frac{\partial \ln c_e^r}{\partial x} \right) + a_s^r F j^r &= 0 \\ \frac{1}{L^r} \frac{\partial}{\partial \tilde{x}} \left(\frac{\kappa_{\text{eff}}^r \bar{\phi}_e^r}{L^r} \frac{\partial}{\partial \tilde{x}} \check{\phi}_e^r + \frac{\kappa_{\text{eff}}^r}{L^r} \frac{2RT(t_+^0 - 1)}{F} \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_e} \right) \frac{\partial \ln \check{c}_e^r}{\partial \tilde{x}} \right) + a_s^r F \tilde{j}^r \check{j}^r &= 0 \\ \frac{\partial}{\partial \tilde{x}} \left(\left[\frac{\kappa_{\text{eff}}^r A \bar{\phi}_e^r}{L^r} \right] \frac{\partial}{\partial \tilde{x}} \check{\phi}_e^r + T \left[\frac{2R(t_+^0 - 1)}{F} \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_e} \right) \frac{\kappa_{\text{eff}}^r A}{L^r} \right] \frac{\partial \ln \check{c}_e^r}{\partial \tilde{x}} \right) + \underbrace{a_s^r A F L^r \tilde{j}^r}_{F} \check{j}^r &= 0.\end{aligned}$$

The nonzero boundary conditions from Eq. (14) are:

$$\begin{aligned}-\kappa_{\text{eff}}^r \left[\frac{\partial}{\partial x} \phi_e^r + \frac{2RT(t_+^0 - 1)}{F} \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_e} \right) \frac{\partial \ln c_e^r}{\partial x} \right] \Big|_{\substack{x=L^n \\ x=L^n + L^s}} &= \frac{i_{\text{app}}}{A} \\ - \left[\frac{\kappa_{\text{eff}}^r A \bar{\phi}_e^r}{L^r} \right] \frac{\partial}{\partial \tilde{x}} \check{\phi}_e^r - T \left[\frac{2R(t_+^0 - 1)}{F} \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_e} \right) \frac{\kappa_{\text{eff}}^r A}{L^r} \right] \frac{\partial \ln \check{c}_e^r}{\partial \tilde{x}} \Big|_{\tilde{x}=1,2} &= i_{\text{app}}.\end{aligned}$$

The initial values are reformulated from Eq. (15) as:

$$\phi_{e,0}^r = -U_{\text{ocp}}^n(\theta_{s,e}^n) \quad \text{and so} \dots \quad \check{\phi}_{e,0}^r = -U_{\text{ocp}}^n(\theta_{s,e}^n) / \bar{\phi}_e^r,$$

where $\theta_{s,e}^r = c_{s,e}^r / c_{s,\text{max}}^r$. We now define

- $\bar{\phi}_e^r = \frac{L^r}{\kappa_{\text{eff}}^r A}$ and $\bar{\kappa}^r = \frac{A \kappa_{\text{eff}}^r}{L^r}$, so $\bar{\phi}_e^r = 1 / \bar{\kappa}^r$.
- $\bar{\kappa}_D = \frac{2R(t_+^0 - 1)}{F} \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_e} \right)$.

This reduces the PDE and its nonzero boundary conditions to

$$\begin{aligned}\frac{\partial}{\partial \tilde{x}} \left(\frac{\partial}{\partial \tilde{x}} \check{\phi}_e^r + T [\bar{\kappa}_D \bar{\kappa}^r] \frac{\partial \ln (\check{c}_e^r)}{\partial \tilde{x}} \right) + F \check{j}^r &= 0 \\ - \frac{\partial}{\partial \tilde{x}} \check{\phi}_e^r - T [\bar{\kappa}_D \bar{\kappa}^r] \frac{\partial \ln (\check{c}_e^r)}{\partial \tilde{x}} \Big|_{\tilde{x}=1,2} &= i_{\text{app}}. \\ \check{\phi}_{e,0}^r &= -U_{\text{ocp}}^n(\theta_{s,e}^n) / \bar{\phi}_e^r.\end{aligned}$$

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

EQUATION IV: MASS CONSERVATION IN THE ELECTROLYTE. We now apply the method to the mass-conservation in electrolyte PDE, Eq. (16):

$$\begin{aligned}\frac{\partial (\varepsilon_e^r c_e^r)}{\partial t} &= \frac{\partial}{\partial x} D_{e,\text{eff}}^r \frac{\partial}{\partial x} c_e^r + a_s^r (1 - t_+^0) j^r \\ \varepsilon_e^r \bar{c}_e^r \frac{\partial \check{c}_e^r}{\partial t} &= \frac{1}{L^r} \frac{\partial}{\partial \tilde{x}} \frac{D_{e,\text{eff}}^r \bar{c}_e^r}{L^r} \frac{\partial}{\partial \tilde{x}} \check{c}_e^r + a_s^r (1 - t_+^0) \tilde{j}^r \check{j}^r \\ \left[\frac{\varepsilon_e^r \bar{c}_e^r A L^r}{1 - t_+^0} \right] \frac{\partial \check{c}_e^r}{\partial t} &= \frac{\partial}{\partial \tilde{x}} \left[\frac{D_{e,\text{eff}}^r A \bar{c}_e^r}{L^r (1 - t_+^0)} \right] \frac{\partial \check{c}_e^r}{\partial \tilde{x}} + \check{j}^r.\end{aligned}$$

The nonzero slope boundary condition at the negative-electrode/separator interface, Eq. (18), is:

$$D_{e,\text{eff}}^n \frac{\partial c_e^n}{\partial x} \Big|_{x=(L^n)^-} = D_{e,\text{eff}}^s \frac{\partial c_e^s}{\partial x} \Big|_{x=(L^n)^+}$$

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

The nonzero slope boundary condition at the separator/positive-electrode interface, Eq. (19), is:

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

The continuity boundary conditions at the electrode/separators boundaries give:

$$\check{c}_e^n|_{\tilde{x}=1^-} = \check{c}_e^s|_{\tilde{x}=1^+}, \quad \text{and} \quad \check{c}_e^s|_{\tilde{x}=2^-} = \check{c}_e^p|_{\tilde{x}=2^+}.$$

The initial values from Eq. (20) are reformulated as:

$$c_e^r(x, 0) = c_{e,0}, \quad \text{and} \quad \check{c}_e^r(\tilde{x}, 0) = \frac{c_{e,0}}{\bar{c}_e^r}.$$

We define $\bar{c}_e^r = c_{e,0}$, which makes $\check{c}_e^r(\tilde{x}, 0) = \check{c}_{e,0}^r = 1$. We further define $\bar{D}_e^r = D_{e,\text{eff}}^r A \bar{c}_e^r / (L^r(1-t_+^0))$. We define $\bar{n}_e^r = \varepsilon_e^r \bar{c}_e^r A L^r / (1-t_+^0)$. Then,

$$\bar{n}_e^r \frac{\partial \check{c}_e^r}{\partial t} = \frac{\partial}{\partial \tilde{x}} \bar{D}_e^r \frac{\partial \check{c}_e^r}{\partial \tilde{x}} + \check{j}^r$$

$$\bar{D}_e^{\text{left}} \frac{\partial \check{c}_e}{\partial \tilde{x}} \Big|_{\text{left}} = \bar{D}_e^{\text{right}} \frac{\partial \check{c}_e}{\partial \tilde{x}} \Big|_{\text{right}},$$

where “left” indicates a point and its corresponding cell region immediately to the left of a separator/electrode interface and “right” indicates a point and its cell region immediately to the right of the same interface. That is, at the negative-electrode/separators interface, left = 1⁻ for the position and left = n for the region; right = 1⁺ for the position and right = s for the region. Similarly, at the separator/positive-electrode interface, left = 2⁻ for the position and left = s for the region and right = 2⁺ for the position and right = p for the region. Then, we can write:

$$\bar{n}_e^r \frac{\partial \check{c}_e^r}{\partial t} = \frac{\partial}{\partial \tilde{x}} \bar{D}_e^r \frac{\partial \check{c}_e^r}{\partial \tilde{x}} + \check{j}^r.$$

It appears that we now need also to find \bar{q}_e^n , \bar{q}_e^s , \bar{q}_e^p , \bar{D}_e^n , \bar{D}_e^s , and \bar{D}_e^p in order to characterize a lithium-ion cell. However, note that there is a relationship between \bar{D}_e^r and $\bar{\kappa}^r$ that we can exploit. Recall the definitions of effective conductivity and diffusivity in terms of the intrinsic conductivity and diffusivity:

$$\begin{aligned} \kappa_{\text{eff}}^n &= \kappa(\varepsilon_e^n)^{\text{brug}}, & D_{e,\text{eff}}^n &= D_e(\varepsilon_e^n)^{\text{brug}} \\ \kappa_{\text{eff}}^s &= \kappa(\varepsilon_e^s)^{\text{brug}}, & D_{e,\text{eff}}^s &= D_e(\varepsilon_e^s)^{\text{brug}} \\ \kappa_{\text{eff}}^p &= \kappa(\varepsilon_e^p)^{\text{brug}}, & D_{e,\text{eff}}^p &= D_e(\varepsilon_e^p)^{\text{brug}}, \end{aligned}$$

where “brug” is the Bruggeman exponent. Therefore,

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

Similarly,

$$\frac{\bar{D}_e^n}{\bar{\kappa}^n} = \frac{\bar{D}_e^s}{\bar{\kappa}^s} = \frac{\bar{D}_e^p}{\bar{\kappa}^p} = \bar{\psi}, \quad (4)$$

and if we have already identified the set of $\bar{\kappa}^r$, then we can compute the set of \bar{D}_e^r by knowing only a single additional parameter, $\bar{\psi}$. In summary, we re-write the PDE, its boundary conditions, and initial condition as

$$\bar{n}_e^r \frac{\partial \check{c}_e^r}{\partial t} = \bar{\psi} \frac{\partial}{\partial \tilde{x}} \bar{\kappa}^r \frac{\partial \check{c}_e^r}{\partial \tilde{x}} + \check{j}^r$$

$$\bar{\kappa}^{\text{left}} \frac{\partial \check{c}_e^r}{\partial \tilde{x}} \Big|_{\text{left}} = \bar{\kappa}^{\text{right}} \frac{\partial \check{c}_e^r}{\partial \tilde{x}} \Big|_{\text{right}}$$

$$\check{c}_e^r|_{\text{left}} = \check{c}_e^r|_{\text{right}}$$

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

Therefore, we now need also to find only \bar{n}_e^n , \bar{n}_e^s , \bar{n}_e^p , and $\bar{\psi}$.

EQUATION V: THE REACTION-KINETICS. Finally, we consider the closure term of the model, expressed via Eqs. (21)–(23). We will not dwell on the details here (but cf. Chap. 2 of [7] for added details at the electrode/electrolyte boundary). For the work we report here, we insert the definitions we have created to this point:

$$\begin{aligned} \check{j}^r &= \check{j}_0^r \left\{ \exp \left(\frac{(1 - \alpha^r)F}{RT} \eta^r \right) - \exp \left(\frac{-\alpha^r F}{RT} \eta^r \right) \right\} \\ \check{j}_0^r &= \frac{k_{\text{norm},0}^r}{\bar{j}^r} (\check{c}_e^r)^{1-\alpha^r} \left(1 - \frac{\check{c}_{s,e}^r}{\bar{c}_{s,\max}^r} \right)^{1-\alpha^r} \left(\frac{\check{c}_{s,e}^r}{\bar{c}_{s,\max}^r} \right)^{\alpha^r} \\ \eta^r &= \bar{\phi}_s^r \check{\phi}_s^r - \bar{\phi}_e^r \check{\phi}_e^r - U_{\text{ocp}}^r (\check{c}_{s,e}^r / \bar{c}_{s,\max}^r) - F [R_f^r \bar{j}^r] j^r. \end{aligned}$$

We define $\bar{k}_0^r = k_{\text{norm},0}^r / \bar{j}^r$ and $\bar{R}_f^r = R_f^r \bar{j}^r$. The additional parameter values we must then estimate are \bar{k}_0^n , \bar{k}_0^p , \bar{R}_f^n , \bar{R}_f^p , $\bar{\phi}_s^n$, $\bar{\phi}_s^p$, α^n and α^p .²

5 Summary of reformulated model equations

The process that we have followed has reduced the number of parameters that must be identified to characterize a physical lithium-ion cell from 36 down to 23 (21 if we assume $\alpha^r = 0.5$). Thirteen “degrees of freedom” have been removed, making the parameter-estimation task mathematically possible in principle using only input/output current/voltage data. The lumped parameters of the reformulated model are summarized in Table 1.

Any similar formulation with the same number of parameters will also be minimal. Since some of the equations of the reformulated model are awkward, we slightly modify them to give a result that is easier to relate directly to the physical processes in the cell. The final notation we develop in this paper is presented in Table 3 and is described below.

We consider first the equations that describe potential in the solid electrodes and the electrolyte. Analyzing the reformulated model shows that the constants $\bar{\phi}_s^r$ and $\bar{\phi}_e^r$ in all applicable cell regions must be estimated to solve for $\check{\phi}_s^r$ and $\check{\phi}_e^r$. Therefore, there is no benefit in converting the variables of the model from ϕ_s^r to $\check{\phi}_s^r$ and from ϕ_e^r to $\check{\phi}_e^r$. We choose to keep the original PDEs in terms of ϕ_s^r and ϕ_e^r but now written in terms of the new lumped-parameter values.

Considering the equations that describe lithium flux and concentrations in the solid electrodes and the electrolyte, we come to a different conclusion. After the reformulation, neither \bar{c}_s^r , \bar{c}_e^r , nor \bar{j}^r appear in the final PDEs, so we do not need to (nor can we) estimate these values from input/output data. So, for now, we will continue to write the corresponding PDEs as functions of \check{c}_s , \check{c}_e , and \check{j} . However, we do note that the “breve” symbol in \check{j} becomes cumbersome, so we rename $\dot{n} = \check{j}$, recognizing that \dot{j} has units of mol s^{-1} and so \dot{n} is a mass flow rate. Recapping, the charge-conservation in the solid equation is presented in the first row of Table 3, where ϕ_s^r is measured in volts and $\bar{\sigma}^r$ in siemens.

For the mass conservation in solid equation, \bar{D}_s^r has units of s^{-1} , which is manageable, but \check{c}_s^r is in mol s^{-1} , which is an awkward unit for concentration. We choose to rewrite its PDE in terms of the already-defined unitless $\theta_s^r = \check{c}_s^r / \bar{c}_{s,\max}^r$, which does not require finding any additional parameter values. For cleaner notation in the charge conservation in electrolyte relationship, we define a unitless ratio of concentrations, $\theta_e^r = \check{c}_e^r$. In these equations, ϕ_e^r is measured in volts, $\bar{\kappa}^r$ in siemens, and t_+^0 is unitless. For the mass conservation in electrolyte relationship, \bar{n}_e is in mol. For the kinetics equation, \bar{k}_0^r is in mol per second, \bar{R}_f^r is in ohms, and η^r is in volts. These modified equations are listed in the remaining four rows of the table.

6 Recovering original electrochemical variables

The reformulated set of PDEs allows us to simulate ϕ_s^r , ϕ_e^r , θ_s^r , θ_e^r , and \dot{n}^r , which is sufficient to be able to compute cell voltage. (This is why it is mathematically possible, in principle, to estimate the required parameter values from current/voltage input/output data.)

However, what if we also desire the ability to simulate c_s^r , c_e^r , and j^r ? This will turn out not to be as necessary as it may seem. For example, cell absolute performance limits $0 \leq c_s^r \leq c_{s,\max}^r$ automatically translate to $0 \leq \theta_s^r \leq 1$ without needing to simulate c_s^r directly or to estimate any new parameter values.

²Sometimes, we assume $\alpha^r = 0.5$, which removes the requirement of finding α^n and α^p .

To recover all original parameter values and electrochemical variables from the modified set, we would need to be able to estimate ten additional values: A , L^n , L^s , L^p , a_s^n , a_s^p , R_s^n , R_s^p , t_{+}^0 , and $c_{e,0}$. It might seem that we should need to estimate thirteen values, since thirteen degrees of freedom have been removed from the model by the reduction process. However, two of those degrees of freedom were removed by noticing the relationship between \bar{D}_e^r and $\bar{\kappa}^r$, which we summarized by replacing three \bar{D}_e^r parameters with a single constant $\bar{\psi}$ in Eq. (4). The remaining degree of freedom was removed by noticing that operational capacity of both electrodes must be equal, which allowed us to replace two $\bar{c}_{s,\max}^r$ parameters with a relationship involving the single constant Q in Eq. (3). Note that most of the ten remaining unknown values are physical dimensions and relatively easy to measure via cell teardown if needed. No elaborate electrochemical techniques are required.

To recover all original electrochemical variables, if we are not concerned with recovering all original parameter values themselves, we would need to determine only eight additional values: $c_{s,\max}^n$, $c_{s,\max}^p$, $c_{e,0}$, a_s^n , a_s^p , L^n , L^p , and A .³ Then, we could compute:

$$c_s^r = c_{s,\max}^r \theta_s^r \quad c_e^r = c_{e,0}^r \theta_e^r; \quad \text{and} \quad j^r = \frac{\dot{n}^r}{a_s^r A L^r}.$$

7 Summary

This paper has presented a procedure for eliminating redundant parameter values from a system of equations. When applied to the DFN PBM of lithium-ion cells, it results in the LPM, for which all parameter values are, in principle, identifiable from input/output measurements.⁴

It is beyond the scope of this paper to present detailed application to nontear-down parameter estimation. However, our research team is preparing a series of articles on this general topic. We have already published methods to estimate the OCP and OCV relationships of a cell [8,9] and on estimating parameter values of the potential and kinetics equations [10]. We are currently preparing manuscripts that show how to find the remaining parameter values using nontear-down methods. We invite the interested reader to explore these works.

Acknowledgments

The information, data, or work presented herein was funded in part by the Advanced Research Projects Agency-Energy (ARPA-E), U.S. Department of Energy, under Award Number DE-AR0000271. We are also grateful for the tutoring of Dr. S. Santhanagopalan from the National Renewable Energy Laboratory.

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³We can combine relationships from Sect. 4 to write: $c_{s,\max}^r = 10\,800Q/(a_s^r A L^r R_s^r F |\theta_{100}^r - \theta_0^r|)$. This replaces the requirement of finding $c_{s,\max}^r$ with the equivalent requirement of finding R_s^r , should they prove simpler to measure.

⁴But, practical identifiability depends on many factors and is still not guaranteed. For example, measurement noise may “drown out” the influence of some parameters on measured voltage and make it very difficult to estimate their values accurately.

Table 1: Parameters in the standard DFN model (left) versus the reformulated LPM (right).

Negative electrode	Separator	Positive electrode		Negative electrode	Separator	Positive electrode
$\sigma_{\text{eff}}^{\text{n}}$		$\sigma_{\text{eff}}^{\text{p}}$		$\bar{\sigma}^{\text{n}}$		$\bar{\sigma}^{\text{p}}$
a_{s}^{n}		a_{s}^{p}		$\bar{\kappa}^{\text{n}}$	$\bar{\kappa}^{\text{s}}$	$\bar{\kappa}^{\text{p}}$
L^{n}	L^{s}	L^{p}		$\bar{D}_{\text{s}}^{\text{n}}$		$\bar{D}_{\text{s}}^{\text{p}}$
$\kappa_{\text{eff}}^{\text{n}}$	$\kappa_{\text{eff}}^{\text{s}}$	$\kappa_{\text{eff}}^{\text{p}}$		$\bar{q}_{\text{e}}^{\text{n}}$	$\bar{q}_{\text{e}}^{\text{s}}$	$\bar{q}_{\text{e}}^{\text{p}}$
D_{s}^{n}		D_{s}^{p}		\bar{k}_0^{n}		\bar{k}_0^{p}
R_{s}^{n}		R_{s}^{p}		$\bar{R}_{\text{f}}^{\text{n}}$		$\bar{R}_{\text{f}}^{\text{p}}$
$\varepsilon_{\text{e}}^{\text{n}}$	$\varepsilon_{\text{e}}^{\text{s}}$	$\varepsilon_{\text{e}}^{\text{p}}$		α^{n}		α^{p}
$D_{\text{e,eff}}^{\text{n}}$	$D_{\text{e,eff}}^{\text{s}}$	$D_{\text{e,eff}}^{\text{p}}$		θ_0^{n}		θ_0^{p}
$k_{\text{norm},0}^{\text{n}}$		$k_{\text{norm},0}^{\text{p}}$		θ_{100}^{n}		θ_{100}^{p}
$c_{\text{s,max}}^{\text{n}}$		$c_{\text{s,max}}^{\text{p}}$		$Q, \bar{\kappa}_D, \text{ and } \bar{\psi} \text{ span all regions}$		
α^{n}		α^{p}				
R_{f}^{n}		R_{f}^{p}				
θ_0^{n}		θ_0^{p}				
θ_{100}^{n}		θ_{100}^{p}				
$A, t_{+}^0, \partial \ln f_{\pm} / \partial \ln c_{\text{e}}, c_{\text{e},0} \text{ span all}$						

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Authors



Dr. Plett received his Ph.D. in Electrical Engineering from Stanford University and is now Professor of Electrical and Computer Engineering at the University of Colorado Colorado Springs. His research focuses on topics in control systems as applied to the management of high-capacity battery systems, such as found in electric vehicles. Current research efforts include: physics-based reduced-order modeling of ideal lithium-ion dynamics and degradation mechanisms; nondestructive parameter estimation for physics-based models; estimation of cell electrochemical and degradation state; state-of-charge and state-of-health estimation; life-extending power-prediction methods.



Dr. Trimboli received his Ph.D. in Control Engineering from Oxford University and is now Associate Professor of Electrical and Computer Engineering at the University of Colorado Colorado Springs. His research focuses on topics in control systems as applied to the management of high-performance battery systems. Current research efforts include: physics-based reduced-order modeling of ideal lithium-ion dynamics; MPC for battery fast-charge and power limit estimation for life extension; battery state estimation using Kalman filters; life-extending power-prediction methods.

Table 2: Summary of the Doyle–Fuller–Newman (DFN) model.

Description	Governing equations	Boundary conditions	Initial conditions
Charge conservation in solid	$\frac{\partial}{\partial x} \sigma_{\text{eff}}^r \frac{\partial}{\partial x} \phi_s^r = a_s^r F j^r \quad (5)$	$\sigma_{\text{eff}}^r \frac{\partial}{\partial x} \phi_s^r \Big _{x=0, L^{\text{tot}}} = \frac{-i_{\text{app}}}{A} \quad (6)$	$\phi_{s,0}^r = U_{\text{ocp}}^r(\theta_{s,0}^r) - U_{\text{ocp}}^n(\theta_{s,0}^n) \quad (8)$
Mass conservation in solid	$\frac{\partial \alpha_s^r}{\partial t} = \frac{1}{\gamma^r} \frac{\partial}{\partial r} \left(D_s^r r^2 \frac{\partial \alpha_s^r}{\partial r} \right) \quad (9)$	$D_s^r \frac{\partial \alpha_s^r}{\partial r} \Big _{r=R_s^r} = -j^r \quad (10)$	$c_{s,0}^r = c_{s,\text{max}}^r (\theta_0^r + z_0(\theta_{100}^r - \theta_0^r)) \quad (11)$
Charge conservation in electrolyte	$\frac{\partial}{\partial x} \left(\kappa_{\text{eff}}^r \frac{\partial}{\partial x} \phi_e^r + \kappa_D^r \frac{\partial \ln c_e^r}{\partial x} \right) + a_s^r F j^r = 0 \quad (12)$	$\left[\kappa_{\text{eff}}^r \frac{\partial}{\partial x} \phi_e^r + \kappa_D^r \frac{\partial \ln c_e^r}{\partial x} \right]_{x=0} = 0 \quad (13)$	$\phi_{e,0}^r = -U_{\text{ocp}}^r(\theta_{s,0}^n) \quad (15)$
Mass conservation in electrolyte	$\kappa_D^r = \frac{2RT\kappa_{\text{eff}}^r(c_e^r - 1)}{F} \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_e} \right)$	$\left[\kappa_{\text{eff}}^r \frac{\partial}{\partial x} \phi_e^r + \kappa_D^r \frac{\partial \ln c_e^r}{\partial x} \right]_{x=L^{\text{tot}}} = \frac{-i_{\text{app}}}{A} \quad (14)$	
		$D_{s,\text{eff}}^r \frac{\partial \alpha_s^r}{\partial x} \Big _{x=0, L^{\text{tot}}} = 0 \quad (17)$	
Mass conservation in electrolyte	$\frac{\partial (c_e^r c_e^s)}{\partial t} = \frac{\partial}{\partial x} D_{e,\text{eff}}^r \frac{\partial}{\partial x} c_e^r + a_s^r (1 - t_+^r) j^r \quad (16)$	$D_{e,\text{eff}}^n \frac{\partial c_e^n}{\partial x} \Big _{x=(L^n)^-} = D_{e,\text{eff}}^s \frac{\partial c_e^s}{\partial x} \Big _{x=(L^n)^+} \quad (18)$	$c_e^r = c_{e,0} \quad (20)$
Kinetics	$j^r = j_0^r \left\{ \exp \left(\frac{(1-\alpha_s^r)F}{RT} \eta^r \right) - \exp \left(\frac{-\alpha_s^r F}{RT} \eta^r \right) \right\} \quad (21)$ $j_0^r = k_{\text{norm},0}^r \left(\left(\frac{c_e^r}{c_{s,0}^r} \right) \left(1 - \frac{c_e^r}{c_{s,\text{max}}^r} \right) \right)^{1-\alpha_s^r} \left(\frac{c_e^r}{c_{s,\text{max}}^r} \right)^{\alpha_s^r} \quad (22)$ $\eta^r = \phi_s^r - \phi_e^r - U_{\text{ocp}}^r(c_{s,e}^r/c_{s,\text{max}}^r) - F R_i^r j^r \quad (23)$	$D_{e,\text{eff}}^s \frac{\partial c_e^s}{\partial x} \Big _{x=(L^n+L^s)^-} = D_{e,\text{eff}}^p \frac{\partial c_e^p}{\partial x} \Big _{x=(L^n+L^s)^+} \quad (19)$	

$x=0$, $x=L^n$, $x=L^n+L^s$, $x=L^{\text{tot}}$ at neg/current-collector, neg/sep, sep/pos, and pos/current-collector boundaries; $r=0$ and $r=R_s$ at particle center and surface. Concentration ratio in solid is $\theta_s = c_s/c_{s,\text{max}}$; potentials in solid and electrolyte are ϕ_s and ϕ_e ; flux from solid to electrolyte is j . “Neg”, “sep” and “pos” denoted by “n”, “s”, and “p”; “r” ∈ {“n”, “s”, “p”}.

Table 3: Summary of the lumped-parameter model (LPM).

Description	Governing equations	Boundary conditions	Initial conditions
Charge conservation in solid	$\sigma^r \frac{\partial^2 \phi_s^r}{\partial \tilde{x}^2} = F \dot{n}^r$	$\sigma^r \frac{\partial}{\partial \tilde{x}} \phi_s^r \Big _{\tilde{x}=0,3} = -i_{\text{app}} \quad (5)$	$\phi_{s,0}^r = U_{\text{ocp}}^r(\theta_{s,0}^r) - U_{\text{ocp}}^n(\theta_{s,0}^n)$
Mass conservation in solid	$\frac{\partial \theta_s^r}{\partial t} = \frac{1}{\gamma^r} \frac{\partial}{\partial \tilde{r}} \left(\tilde{D}_s^r \tilde{r}^2 \frac{\partial \theta_s^r}{\partial \tilde{r}} \right)$	$\tilde{D}_s^r \frac{\partial \theta_s^r}{\partial \tilde{r}} \Big _{\tilde{r}=1} = -\frac{ \theta_{100}^r - \theta_0^r }{3Q} \dot{n}_t^r \quad (6)$	$\theta_{s,0}^r = \theta_0^r + z_0(\theta_{100}^r - \theta_0^r)$
Charge conservation in electrolyte	$\frac{\partial}{\partial \tilde{x}} \left(\tilde{\kappa}^r \left(\frac{\partial}{\partial \tilde{x}} \phi_e^r + \tilde{\kappa}_D^r T \frac{\partial \ln(\theta_e^r)}{\partial \tilde{x}} \right) \right) + F \dot{n}^r = 0$	$\tilde{\kappa}^r \left[\frac{\partial}{\partial \tilde{x}} \phi_e^r + \tilde{\kappa}_D^r T \frac{\partial \ln(\theta_e^r)}{\partial \tilde{x}} \right]_{\tilde{x}=1,2} = -i_{\text{app}} \quad (7)$	$\phi_{e,0} = -U_{\text{ocp}}^r(\theta_{s,0}^n)$
Mass conservation in electrolyte	$\dot{n}_e^r \frac{\partial \theta_e^r}{\partial t} = \tilde{\psi} \frac{\partial}{\partial \tilde{x}} \tilde{\kappa}^r \frac{\partial}{\partial \tilde{x}} \theta_e^r + \dot{n}^r$	$\tilde{\kappa}^r \frac{\partial \theta_e^r}{\partial \tilde{x}} \Big _{\tilde{x}=1-} = \tilde{\kappa}^r \frac{\partial \theta_e^r}{\partial \tilde{x}} \Big _{\tilde{x}=1+} \quad (8)$	$\theta_{e,0} = 1$
Kinetics	$\dot{n}^r = \dot{n}_0^r \left(\exp \left(\frac{(1-\alpha_s^r)F}{RT} \eta^r \right) - \exp \left(\frac{-\alpha_s^r F}{RT} \eta^r \right) \right)$ $\dot{n}_0^r = \tilde{k}_0^r (\theta_e^r)^{1-\alpha_s^r} (1 - \theta_{ss}^r)^{1-\alpha_s^r} (\theta_{ss}^r)^{\alpha_s^r}$ $\eta^r = \phi_s^r - \phi_e^r - U_{\text{ocp}}^r(\theta_{ss}^r) - F R_i^r \dot{n}^r$	$\tilde{\kappa}^r \frac{\partial \theta_e^r}{\partial \tilde{x}} \Big _{\tilde{x}=0,3} = 0 \quad (9)$	

$\tilde{x}=0$, $\tilde{x}=1$, $\tilde{x}=2$, $\tilde{x}=3$ at neg/current-collector, neg/sep, sep/pos, and pos/current-collector boundaries; $\tilde{r}=0$ and $\tilde{r}=1$ at particle center and surface. Concentration ratios in solid and electrolyte are $\theta_s = c_s/c_{s,\text{max}}$ and $\theta_e = c_e/c_{e,0}$; potentials in solid and electrolyte are ϕ_s and ϕ_e ; flux from solid to electrolyte is $\dot{n} = a_s A L j$. “Neg”, “sep” and “pos” denoted by “n”, “s”, and “p”; “r” ∈ {“n”, “s”, “p”}.