OPEN ACCESS

An Efficient Electrochemical-Thermal Tanks-in-Series Model for Lithium-Ion Batteries

To cite this article: Akshay Subramaniam et al 2020 J. Electrochem. Soc. 167 113506

View the article online for updates and enhancements.
An Efficient Electrochemical-Thermal Tanks-in-Series Model for Lithium-Ion Batteries
Akhshay Subramaniam,1,* Suryanarayana Kolluri,2,* Shriram Santhanagopalan,3,*** and Venkat R. Subramanian2,****

1Department of Chemical Engineering, University of Washington, Seattle, Washington 98195, United States of America
2Walker Department of Mechanical Engineering & Material Science Engineering, Texas Materials Institute, The University of Texas at Austin, Austin, Texas 78712, United States of America
3Transportation and Hydrogen Systems Center, National Renewable Energy Laboratory, Golden, Colorado 80401, United States of America

This article extends the Tanks-in-Series methodology (J. Electrochem. Soc., 167, 013534 (2020)) to generate an electrochemical-thermal model for Li-ion batteries. Energy balances based on porous electrode theory, including flux and generation terms, are volume-averaged for each region in a cathode-separator-anode representation, including current collectors. The original Tank model is thus augmented by a volume-averaged energy balance in each region, containing source terms and interfacial heat fluxes that are approximated accordingly. Cell-level quantities and temperature predictions are evaluated against a pseudo 2-dimensional (p2D) model. Acceptable voltage errors are achieved for relatively aggressive conditions of discharge and external heat transfer. Predictions of electrochemical variables are examined, and implications of the approximations discussed. The simplified methodology is also demonstrated for examples of large-scale models used in studying practical cell configurations. The Tanks-in-Series approach leads to a substantial reduction in equation system size, with attendant savings in computation time. This suggests potential in applications such as optimal charging, cell-balancing and estimation, and aids efforts to incorporate electrochemical models in advanced Battery Management Systems.

© 2020 The Author(s). Published on behalf of The Electrochemical Society by IOP Publishing Limited. This is an open access article distributed under the terms of the Creative Commons Attribution Non-Commercial No Derivatives 4.0 License (CC BY-NC-ND, http://creativecommons.org/licenses/by-nc-nd/4.0/), which permits non-commercial reuse, distribution, and reproduction in any medium, provided the original work is not changed in any way and is properly cited. For permission for commercial reuse, please email: permissions@ioppublishing.org. [DOI: 10.1149/1945-7111/aba700]

List of symbols

<table>
<thead>
<tr>
<th>Dependent Variables</th>
<th>Other Symbols</th>
</tr>
</thead>
<tbody>
<tr>
<td>(c) Electrolyte Concentration</td>
<td>(V_{cell}) Cell Voltage</td>
</tr>
<tr>
<td>(c^s) Solid Phase Concentration</td>
<td>(j) Pore-wall flux</td>
</tr>
<tr>
<td>(\phi_l) Liquid Phase Potential</td>
<td>(N) Electrolyte molar flux</td>
</tr>
<tr>
<td>(\phi_s) Solid Phase Potential</td>
<td>(q) Heat flux</td>
</tr>
<tr>
<td>(T) Temperature</td>
<td>(Q_{rev}) Reversible volumetric heat generation rate</td>
</tr>
<tr>
<td>(Q_{irrev}) Irreversible volumetric heat generation rate due to interfacial polarization</td>
<td>(Q_{voluc}) Volumetric heat generation rate due to ohmic drop</td>
</tr>
<tr>
<td>(\beta) Ratio of the instantaneous current density to the nominal average for a given cell in a multi-cell system</td>
<td>(h) Ambient heat transfer coefficient</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Other Subscripts</th>
<th>Other Superscripts</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Pertaining to region (i) where (i \in {0, 1, 2, 3, 4})</td>
<td>(s, \text{avg}) Pertaining to the average over the volume of the solid particle</td>
</tr>
<tr>
<td>(ij) Pertaining to the interface between regions (i) and (j), where (i, j \in {0, 1, 2, 3, 4})</td>
<td>(s, \text{surf}) Pertaining to the surface of the particle in the solid phase</td>
</tr>
<tr>
<td>(i,ij) Pertaining to the interface between regions (i) and (j) on the side of region (i) where (i, j \in {0, 1, 2, 3, 4})</td>
<td>(i, \text{avg}) Pertaining to the average over the volume of a porous domain</td>
</tr>
<tr>
<td>(i,k) Pertaining to the region (i) of the (k)th cell in an N-cell stack, where (i \in {0, 1, 2, 3, 4}) and (1 \leq k \leq N_{cell})</td>
<td>(-)</td>
</tr>
</tbody>
</table>

Lithium-ion (Li-ion) batteries are achieving increasing ubiquity as Electric Vehicle (EV) adoption continues to grow. In this context, further improvement in competitiveness relative to internal combustion engines entails extracting the maximum possible value out of battery systems by ensuring their safe and efficient operation. The performance and safety issues of Li-ion batteries are well-known, and problems such as Lithium plating,2,4,5 chemomechanical degradation6 and thermal runaways7 are exacerbated under practical conditions such as fast charging, low ambient temperatures, and dynamic operation. In multi-cell stacks, large format cells and large battery packs, spatial non-uniformities in temperature greatly influence the electrochemical performance of individual cells, with significant implications for overall utilization, temperature, safety and system lifetime.8–11 Advanced Battery Management Systems (BMS) and Thermal Management Systems (TMS) designed to ensure optimal operation have access to a limited number of measurements, and rely on the predictions of key quantities such as State of Charge (SoC), State of Health (SoH), voltage-current trends, and temperature distributions.12 To this end, mathematical models play a critical role in predicting battery state and dynamics, which in turn informs estimation, optimization and real-time control strategies.13–17 Prediction of thermal dynamics is particularly critical in view of deleterious phenomena such as overheating, non-uniform capacity degradation, and potential thermal runaways.18

The choice of battery model is typically a trade-off between physical detail and computational speed. Various approximation and reformulation techniques have been applied to enable the
practicability of complex electrochemical models by reducing their computational demands.\textsuperscript{20} A relatively simple method for the generation of efficient electrochemical-thermal models is to couple the classic Single Particle Model (SPM) with a lumped description of thermal dynamics. Simple thermal models are generated based on the form-factor of the cell, and approximations made for the various contributions to the electrochemical heat generation rates. These methods have been demonstrated for various systems-level applications.\textsuperscript{1,21} Often the thermal model computes heat source from more complex electrochemical model while using a simple series-resistor model for thermal transport.\textsuperscript{22} While these models have significantly improved computational efficiency, they are only valid for specific operating regimes and parameter combinations, and are unable to account for subtle electrochemical aspects that impact battery state. Additionally, while SPM-like models can neglect electrolyte dynamics in isothermal situations, the non-linear dependence of electrolyte transport on temperature necessitates incorporation of equations for the electrolyte, which can often require ad-hoc simplifications, such as empirical equations,\textsuperscript{23} uniform reaction distributions\textsuperscript{14} or polynomial spatial profiles.\textsuperscript{25} Analytical solutions for the temperature profiles can also be derived under certain limiting conditions, but their accuracy is also similarly restricted and relies on simplifying assumptions on either the electrochemical or thermal model components.

Model reformulation techniques achieve computationally efficient simulations while retaining the full order of the p2D model. Our group and others have demonstrated reformulated models for coupled electrochemical-thermal dynamics chiefly using polynomial-profile techniques for solid phase transport, and collocation and Galerkin methods along the electrode thickness.\textsuperscript{24-27} However, while ~ms computation times have been demonstrated for a single-cell “sandwich” representation, computational efficiency may be compromised for multi-cell stacks, particularly in situations of non-uniform temperature or current density, which result in asymmetric boundary conditions that increase the computational burden.\textsuperscript{25} The computational performance of reformulated models for long cycling simulations also needs to be evaluated. Additionally, parameterization of such models is a non-trivial task.

In addition to the spatial variations along the electrode thickness predicted by p2D models (Fig. 1), large format cells such as those considered for EVs exhibit spatial non-uniformities in the plane of their current collectors (y−z plane).\textsuperscript{28} These effects depend on design factors such as the location of collector tabs, cooling conditions, and contact and thermal resistances.\textsuperscript{29-31} A realistic model for design and safety entails computing the temperature and current distributions in the collectors, which in turn affects the local electrochemical behavior within the electrode thickness. This requires a coupled modeling approach in which the local potential, temperature, and current density is used as input to an electrochemical model in the x-direction at each point in the collector plane. Given the computational complexity of such a Multi-Scale Multi-Domain (MSMD) framework where the electrochemical model is evaluated at every point in a 2 or 3-dimensional computational grid, efficient electrochemical models for the “electrode subdomains” have received significant attention.\textsuperscript{29,32} While examples of efficient reformulated SPM models exist,\textsuperscript{29} usually reduced order models are employed. Various approaches such as equivalent circuit models,\textsuperscript{28} extended SPM,\textsuperscript{33} Pade approximation models,\textsuperscript{33} and series expansions\textsuperscript{28} have been applied. While these approaches significantly reduce the computational footprint of coupled MSMD models, several works use a volume-averaged approach in which temperature variations along the x thickness dimension are neglected.\textsuperscript{29,34-37} Lumped thermal models are used even when standard and reformulated implementations of the p2D models are used for the electrochemical submodels.\textsuperscript{35} And even when the p2D model is used to model full cells.\textsuperscript{32,39} For a single cathode—separator—anode representation, the ambient heat transfer coefficients and length scales for thermal conduction are low enough that the Biot numbers Bi satisfy the thresholds (Bi < 0.1) for uniform temperature.\textsuperscript{40} However, these assumptions may not hold if the Biot number exceeds the threshold, as is possible with large cell stacks and multiple cell layers.\textsuperscript{41} Significant temperature gradients may also result for aggressive convective heat transfer conditions and due to the presence of interfacial thermal resistances.\textsuperscript{31,39} A common approach to account for gradients in a multi-cell stack is to assume a uniform temperature within each individual cell and make suitable approximations for the flux at intercell interfaces,\textsuperscript{30,41} but this approach may also be error-prone if intra-cell gradients are significant. To circumvent the need for p2D models for multi-cell stacks, efficient analytical solutions have been developed using rigorous asymptotic analyses,\textsuperscript{30} but their accuracy is similarly restricted to low Bi regimes.

In adaption to design and analysis applications, we can also use the electrochemical information provided by such models to compute cell-level quantities that are of salience in real-time BMS and TMS applications. As mentioned previously, cell-balancing is a critical function of BMS. The performance of multi-cell stacks and large battery packs consisting of series-parallel combinations of cells is often limited by the “weakest” cell in the array.\textsuperscript{9,18} The BMS must be able to ensure that individual cells are not over-charged or over-discharged and ensure that individual cells are not over or under-loaded, thereby mitigating the effects of non-uniform degradation rates.\textsuperscript{3} This requires the monitoring of the State of Charge (SoC) of individual cells and estimates of the current flowing through each cell. In real-time applications, this is often done by assuming empirical circuit models for each cell,\textsuperscript{15} in which the temperature also thought to affect individual cell resistances and heat generation rates, which in turn alters the effective resistance of each cell and thus the dynamic current distribution.\textsuperscript{10} In contrast to ad-hoc empirical models, physics-based models can leverage the full electrochemical state to directly compute instantaneous SoC and current in individual cells, thereby capturing the complex interplay of various electrochemical phenomena that influence the dynamic behavior of cell resistance. In most cases, the p2D model is far too computationally expensive to simulate multiple cells in real-time, not including the additional computational overhead of using the simulation results to compute emergent cell-level quantities. However, a simplified model which still retains adequate electrochemical information can potentially help balance this trade-off.

The Tanks-in-Series methodology was previously introduced and applied to the isothermal p2D model.\textsuperscript{42} This approach involves the rigorous volume-averaging of each conservation law in a given domain, followed by suitable approximations of interfacial fluxes for closure. Such an approach thus obviates the need for uniform temperature assumptions by way of physically meaningful approximations for the gradients, which can capture temperature drops due to thermal resistances and in multi-cell stacks. Additionally, the flux approximations may be easily refined by variation of the corresponding diffusion lengths, providing a flexible way for tuning the gradients within each domain, and suggesting applications in parameter estimation. Since each partial differential equation (PDE) in the p2D model is replaced by its volume-averaged form, a single cell can be represented by <20 Differential Algebraic Equations (DAEs). Based on our past work, this suggests substantial gains in computational efficiency (∼1 s computation time) for a multi-cell stack featuring ∼500 DAEs,\textsuperscript{26} and makes the Tanks-in-Series method worthy of consideration.

Beginning with the formulation of the Thermal Tanks-in-Series method for the electrochemical-thermal p2D model, the article examines the predictions of the Tanks-in-Series model with respect to the p2D model for representative cases of galvanostatic discharge and external heat transfer. Results are also presented for a second parameter set for which more significant electrolyte phase resistances are expected. Subsequently, we define a case study of a multi-cell stack with asymmetric temperature boundary conditions and sub-zero ambient temperatures, which represents a sufficiently non-uniform temperature distribution scenario for evaluating our Tank Models. Pertinent parameters such as the number of cells, the Biot number, and discharge rate are then varied, and the predictions and
performance metrics of the Tanks-in-Series model examined as a function of increasing temperature non-uniformity. The ability of the Tanks-in-Series model to compute cell-level quantities is also demonstrated, and its accuracy is evaluated against a multi-cell p2D model. The computational performance of the model is then briefly discussed, concluding with a short discussion on possible applications, limitations, and future work.

**Model Development**

**Single cell model**—In this section, we apply the Tanks-in-Series methodology to the governing equations for temperature in the p2D thermal model. The modeling schematic of a single repeat cell “sandwich,” also called a “single cell,” is depicted in Fig. 1. The complete set of equations and boundary conditions used in this study may be found in Table I. The full-order model used as the benchmark in this study is based on the extensions to the isothermal p2D model by Newman and others.

Energy balance equation: volume-averaging.—In the positive electrode, the governing PDE for the temperature \( T \) is given by

\[
\rho_1 C_{p1} \frac{\partial T_1}{\partial t} = -\frac{\partial q_1}{\partial x} + Q_{rev,1} + Q_{rev,1} + Q_{ohmic,1}[l_0 < x < l_0 + l_1]
\]  

For one spatial dimension in cartesian coordinates, \( q_i \) denotes the local heat flux, and \( Q_{rev,1}, Q_{rev,1} \) and \( Q_{ohmic,1} \) denote the volumetric source terms corresponding to reversible and irreversible components of the heat of reaction, and joule heating resulting from ohmic effects. \( \rho_i \) and \( C_{pi} \) respectively denote the density and heat capacity of the material in domain \( i \).

Due to the absence of solid active material, the conservation equation for \( T \) in the separator is characterized by a lack of heat of reaction terms as

\[
\rho_2 C_{p2} \frac{\partial T_2}{\partial t} = -\frac{\partial q_2}{\partial x} + Q_{ohmic,2}[l_0 + l_1 < x < l_0 + l_1 + l_2]
\]  

The subscript 2 is used to denote the variables in the separator domain.

The equation for the negative electrode is identical in form to that of the positive electrode

\[
\rho_3 C_{p3} \frac{\partial T_3}{\partial t} = -\frac{\partial q_3}{\partial x} + Q_{rev,3} + Q_{rev,3} + Q_{ohmic,3}[l_0 + l_1 < x < l_0 + l_1 + l_2 + l_3] \tag{3}
\]

\( q_1, q_2, q_3 \) are local thermal fluxes which may be defined using standard constitutive equations. Thus we have

\[
q_i = -\lambda_i \frac{\partial T_i}{\partial x} \tag{4}
\]

In the above equations, \( \lambda_i \) denotes the (assumed isotropic) thermal conductivity of the domain \( i \).

For the thermal model, we also consider the temperature distribution through the current collectors. For the positive electrode, the governing equation for the Aluminum current collector (Region 0 in Fig. 1) may be written as

\[
\rho_0 C_{p0} \frac{\partial T_0}{\partial t} = -\frac{\partial q_0}{\partial x} + \frac{i_{app}^2}{\sigma_0}[0 < x < l_0] \tag{5}
\]

Similarly, for the negative Copper (Cu) collector, Region 4 (Fig. 1) may be written as

\[
\rho_4 C_{p4} \frac{\partial T_4}{\partial t} = -\frac{\partial q_4}{\partial x} + \frac{i_{app}^2}{\sigma_4}[l_0 + l_1 + l_2 + l_3 < x < l_0 + l_1 + l_2 + l_3] \tag{6}
\]

Note that the only source term in the current collectors is ohmic heating due to the passage of current.

For the base case, the boundary conditions are imposed at the surface of the current collectors as

\[
\frac{\partial T}{\partial x} = \frac{\partial T}{\partial x} = 0 \text{ at } x = 0, x = l_0, x = l_0 + l_1, x = l_0 + l_1 + l_2, x = l_0 + l_1 + l_2 + l_3, x = l_0 + l_1 + l_2 + l_3 + l_4
\]
Table I. Governing Equations for the electrochemical-thermal p2D model.

Equations

<table>
<thead>
<tr>
<th>Region</th>
<th>Equations</th>
<th>Boundary Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positive Current Collector (Region 0)</td>
<td>[ \rho_0 C_p \frac{\partial T_0}{\partial t} - \frac{\partial}{\partial x} \left( D(c_1) \frac{\partial}{\partial x} \right) + \frac{\partial}{\partial x} \left( \frac{\rho \sigma_0}{a_0} \right) ]</td>
<td>[ \lambda_0 \frac{\partial T_0}{\partial x} \bigg</td>
</tr>
<tr>
<td>Positive Electrode (Region 1)</td>
<td>[ \frac{\partial}{\partial t} \left[ \frac{\partial}{\partial x} \right] \left[ D(\epsilon_1) \frac{\partial}{\partial x} \right] + a_1 (1 - i_0) j_i ]</td>
<td>[ \frac{\partial}{\partial x} \left[ \frac{\partial}{\partial x} \right] = 0 ]</td>
</tr>
<tr>
<td></td>
<td>[ i_{1,1} = -\kappa(c_1) \epsilon_1^b \frac{\partial \phi_{1,1}}{\partial x} + \frac{2RT (1 - \epsilon_1^b)}{F} \left( 1 + \frac{\partial \ln f}{\partial \ln \epsilon_1} \right) \kappa(c_1) \epsilon_1^b \frac{1}{\epsilon_1} \frac{\partial}{\partial x} ]</td>
<td>[ \frac{\partial^2}{\partial x^2} \frac{\partial}{\partial x} \bigg</td>
</tr>
<tr>
<td></td>
<td>[ \frac{\partial}{\partial x} \left[ \frac{\partial}{\partial x} \right] = \frac{i_{1,1}}{a_1 F_j} ]</td>
<td>[ \frac{\partial}{\partial x} \left[ \frac{\partial}{\partial x} \right] \bigg</td>
</tr>
<tr>
<td></td>
<td>[ \frac{\partial}{\partial t} \left[ \frac{\partial}{\partial x} \right] = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 D_j \frac{\partial}{\partial r} \right] ]</td>
<td>[ \frac{\partial}{\partial x} \left[ \frac{\partial}{\partial x} \right] \bigg</td>
</tr>
<tr>
<td>Separator (Region 2)</td>
<td>[ \epsilon_2 \frac{\partial c_2}{\partial t} = \frac{\partial}{\partial x} \left[ D(c_2) \epsilon_2 \frac{\partial}{\partial x} \right] ]</td>
<td>[ \frac{\partial}{\partial x} \left[ \frac{\partial}{\partial x} \right] \bigg</td>
</tr>
<tr>
<td></td>
<td>[ i_{2,3} = -\kappa(c_2) \epsilon_2^b \frac{\partial \phi_{2,3}}{\partial x} + \frac{2RT (1 - \epsilon_2^b)}{F} \left( 1 + \frac{\partial \ln f}{\partial \ln \epsilon_2} \right) \kappa(c_2) \epsilon_2^b \frac{1}{\epsilon_2} \frac{\partial}{\partial x} ]</td>
<td>[ \frac{\partial}{\partial x} \left[ \frac{\partial}{\partial x} \right] \bigg</td>
</tr>
<tr>
<td>Negative Electrode (Region 3)</td>
<td>[ \epsilon_3 \frac{\partial c_3}{\partial t} = \frac{\partial}{\partial x} \left[ D(c_3) \epsilon_3 \frac{\partial}{\partial x} \right] + a_3 (1 - i_3) j_3 ]</td>
<td>[ \frac{\partial}{\partial x} \left[ \frac{\partial}{\partial x} \right] \bigg</td>
</tr>
<tr>
<td></td>
<td>[ i_{3,3} = -\kappa(c_3) \epsilon_3^b \frac{\partial \phi_{3,3}}{\partial x} + \frac{2RT (1 - \epsilon_3^b)}{F} \left( 1 + \frac{\partial \ln f}{\partial \ln \epsilon_3} \right) \kappa(c_3) \epsilon_3^b \frac{1}{\epsilon_3} \frac{\partial}{\partial x} ]</td>
<td>[ \frac{\partial}{\partial x} \left[ \frac{\partial}{\partial x} \right] \bigg</td>
</tr>
<tr>
<td></td>
<td>[ \frac{\partial}{\partial x} \left[ \frac{\partial}{\partial x} \right] = a_3 F_j ]</td>
<td>[ \frac{\partial}{\partial x} \left[ \frac{\partial}{\partial x} \right] \bigg</td>
</tr>
<tr>
<td></td>
<td>[ \frac{\partial}{\partial t} \left[ \frac{\partial}{\partial x} \right] = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 D_j \frac{\partial}{\partial r} \right] ]</td>
<td>[ \frac{\partial}{\partial x} \left[ \frac{\partial}{\partial x} \right] \bigg</td>
</tr>
<tr>
<td></td>
<td>[ \rho_3 C_p \frac{\partial T_3}{\partial t} = \frac{\partial}{\partial x} \left[ \rho_3 \frac{\partial T_3}{\partial x} \right] + Q_{\text{nat},3} + Q_{\text{rev},3} + Q_{\text{soln},3} ]</td>
<td>[ \frac{\partial}{\partial x} \left[ \frac{\partial}{\partial x} \right] \bigg</td>
</tr>
</tbody>
</table>
For the one-dimensional model in Cartesian coordinates, the differential volume $dV$ is given by $dV = Adx$, where $A$ is a constant that may be considered a cross-sectional area. In addition, we express the integrals in terms of average quantities such as,

$$T_i = \frac{\int_{v_i} T_{rev} dv}{\int_{v_i} dv} \quad \text{and} \quad \bar{Q}_{rev,1} = \frac{\int_{v_i} Q_{rev,1} dv}{\int_{v_i} dv} \quad \text{with} \quad v \text{ denoting the volume average of variable } v \text{ in a given “tank.”}$$

Substituting these relations converts the volume integral into a one-dimensional integral over electrode thickness, i.e., from $x = 0$ to $x = l_i$.

Equation 14 thus becomes

$$\rho_i C_{p_i} \frac{dT_i}{dt} = \left( \frac{q_{1,x=0} - q_{1,x=L_1}}{l_1} \right) + Q_{rev,1} + Q_{ohmic,1} + Q_{rev,1}$$

Similarly equivalent derivations may be obtained for the other domains as follows

$$\rho_i C_{p_i} \frac{dT_i}{dt} = \left( \frac{q_{3,x=0} - q_{3,x=L_3}}{l_3} \right) + Q_{rev,3} + Q_{ohmic,3} + Q_{rev,3}$$

Source term approximations.—The volume-averaged heat generation terms due to electrochemical reaction are defined using standard approximations of the Tanks-in-Series approach as

$$\bar{Q}_{rev,1} = \left( \frac{i_{app,1}}{l_1} \right) \left( \frac{\phi_{i,1} - \phi_{i,1}}{U(c_i^{surf})} \right) \quad \text{i.e., } i \in \{1, 3\}$$

The averaged form of the ohmic contributions is given by

$$\bar{Q}_{ohmic} = \left( \frac{i_{app,1}}{l_1} \right) \left( \frac{\phi_{i,1} - \phi_{i,1}}{U(c_i^{surf})} \right) \quad \text{i.e., } i \in \{1, 3\}$$

A detailed derivation of the $-Q_{\text{ohmic},i}$ terms may be found in the Appendix.

Recalling the standard flux approximations introduced in previous work, \cite{41,43} we have

### Table I. (Continued).

<table>
<thead>
<tr>
<th>Equations</th>
<th>Boundary Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_i C_{p_i} \frac{dT_i}{dt} = \frac{\partial q_{i,x=L_1}}{\partial x} \left[ \lambda_i \frac{\partial T_i}{\partial x} \right] + \frac{i_{app}^i}{\sigma_i} \left[ \right]$</td>
<td>$\lambda \frac{dT_i}{dx}</td>
</tr>
</tbody>
</table>

In addition, we also impose continuity conditions for temperature and heat fluxes at the interfaces between the separator and electrodes, and the electrodes and collectors. At the positive electrode-separator interface, this is expressed as

$$T_{1,x=L_1 + L_2} = T_{2,x=L_1 + L_2} \quad q_{1,x=L_1 + L_2} = q_{2,x=L_1 + L_2}$$

Similarly, at the interface between the separator and negative electrode, we have

$$T_{2,x=L_1 + L_2} = T_{3,x=L_1 + L_2} \quad q_{2,x=L_1 + L_2} = q_{3,x=L_1 + L_2}$$

At the collector-electrode interfaces, we have

$$T_{0,x=L_1} = T_{1,x=L_1} \quad q_{0,x=L_1} = q_{1,x=L_1} = q_{01}$$

$$T_{3,x=L_1 + L_2 + L_3} = T_{4,x=L_1 + L_2 + L_3} \quad q_{3,x=L_1 + L_2 + L_3} = q_{4,x=L_1 + L_2 + L_3}$$

Note that in the above equations we neglect any interfacial thermal resistances at the separator-electrode interfaces.

Within the porous domains, the volumetric heat generation terms are defined as \cite{37,46}

$$Q_{rev,i} = F a_i \left( \phi_{i} - \phi_{i} \right) - U(c_i^{surf}) \quad i \in \{1, 3\}$$

$$Q_{ohmic,i} = \sigma_i (1 - \epsilon_i - \epsilon_{f}) \left( \frac{\partial \phi_{i}}{\partial x} \right)^2 + \left( \kappa_i \epsilon_i^{b} \right) \left( \frac{\partial \phi_{i}}{\partial x} \right)^2$$

$$- 2 \kappa_i \epsilon_i^{b} \left( 1 - \frac{\alpha_i}{\epsilon_i} \right) R T_i \left( \frac{\partial \phi_{i}}{\partial x} \right) \left( \frac{\partial \ln f}{\partial \ln c_i} \right) \left( \frac{\partial \ln c_i}{\partial x} \right) \left( \right) \times i \in \{1, 2, 3\}$$

Now, assuming constant density and heat capacities, Eq. 1 is integrated over the volume of the positive electrode $V_i$ as

$$\rho_i C_{p_i} \int_{V_i} T_i dV \quad \frac{dt}{dt} = - \int_{V_i} \frac{q_{i,x=L_1}}{V_i} dV$$

$$+ \int_{V_i} Q_{rev,i} dV + \int_{V_i} Q_{ohmic,i} dV$$

$$+ \int_{V_i} Q_{surf,i} dV \quad [14]$$

For the ohmic heating term, we have, using the constitutive equations for electrolyte-phase current from Ref. 43

$$Q_{ohmic,i} = \sigma_i \left( 1 - \epsilon_i - \epsilon_{f} \right) \left( \frac{\partial \phi_{i}}{\partial x} \right)^2 + \left( \kappa_i \epsilon_i^{b} \right) \left( \frac{\partial \phi_{i}}{\partial x} \right)^2$$

$$- 2 \kappa_i \epsilon_i^{b} \left( 1 - \frac{\alpha_i}{\epsilon_i} \right) R T_i \left( \frac{\partial \phi_{i}}{\partial x} \right) \left( \frac{\partial \ln f}{\partial \ln c_i} \right) \left( \frac{\partial \ln c_i}{\partial x} \right) \left( \right) \times i \in \{1, 2, 3\}$$

Now, assuming constant density and heat capacities, Eq. 1 is integrated over the volume of the positive electrode $V_i$ as
\[ q_{ij} = -\lambda_j \frac{\partial T_j}{\partial x} \approx \lambda_j \left( \frac{\Delta T_j}{\delta T_{ij,j}} \right) = \lambda_j \left( \frac{T_j - T_{ij}}{l_j} \right) \]

\[ q_{ij} = -\lambda_j \frac{\partial T_j}{\partial x} \approx \lambda_j \left( \frac{\Delta T_j}{\delta T_{ij,j}} \right) = -\lambda_j \left( \frac{T_j - T_{ij}}{l_j} \right) \quad [23] \]

Here we have implicitly used the flux continuity conditions of Eqs. 8–10, which then allows us to estimate the unknown interfacial value as

\[ \lambda_j \left( \frac{T_j - T_{ij}}{l_j} \right) = -\lambda_j \left( \frac{T_j - T_{ij}}{l_j} \right) \]

\[ T_{ij} = \frac{\lambda_j}{l_j} T_j + \frac{\lambda_j}{l_j} T_i \quad [24] \]

Now, after substituting Eq. 24 into the volume-averaged Eqs. 16–18, we obtain the final form of the temperature equations. These equations constitute the thermal augmentation to the isothermal Tank Model equations of Ref. 43. Taken together, the combined set of equations is termed the “Thermal Tank Model.” The complete set of equations for the porous domains may be found in Table V. Figure 2 represents the modeling schematic of the Tanks-in-Series representation of a single cell.

Multi-cell stack model.—We now briefly describe the extension of the single cell models of the previous section to a simplified multi-cell stack depicted in Fig. 3. As before, each model layer is represented as a multi-layer pouch cell, in which the individual layers are connected in parallel. Each individual layer may be regarded a “repeat unit,” itself represented by an electrochemical model for a single cell.29,38,41,42 Given that a single domain consists of five volumes, the volume-averaged Tanks-in-Series model results in five such tanks. Thus a 10-cell stack may thus be regarded as “50 Tanks-in-Series.” Figure 3 indicates that adjacent cells are in thermal contact and can exchange heat by conduction. Appropriate coupling boundary conditions need to be defined to account for this thermal interaction.25,38 In addition, the cell draws a total current which is distributed among the individual layers, which are connected electrically in parallel and thus experience the same voltage \( V_{cell} \).

For the positive collector, the temperature coupling boundary conditions between successive cells, thermally in series, are given by

\[ T_{k,x=0} = T_{k+1,x=0} + \frac{l_0 + l_1 + l_2 + l_3 + l_4}{2}, \quad \frac{\partial T_{k+1,x=0}}{\partial x} = \frac{\partial T_{k,x=0}}{\partial x} \quad [1 \leq k \leq N_{cell}] \]

Here we note that each “repeat unit” includes one half of each current collector, as indicated in Fig. 3.

Similarly, at the negative Cu collectors in the interior layers, we have

\[ T_{k,x=0} = T_{k+1,x=0} \]

\[ \frac{\partial T_{k+1,x=0}}{\partial x} = \frac{\partial T_{k,x=0}}{\partial x} \quad [2 \leq k \leq N_{cell} - 1] \quad [26] \]

Where the gradient boundary condition is required based on the modeling approach described above. This is essentially a flux continuity condition, with the negative sign required by the coordinate transformation approach.25 For the Cu collectors for the end cells in Fig. 3, for the leftmost “hot” cell, we have the following boundary conditions for \( T_0 \)

\[ T_{0,1,x=0} = T_{cont} \quad [27] \]

This denotes the constant temperature boundary condition at the left end, as indicated in Fig. 3. In this case, the subscript \( k = 1 \) denotes for the first cell.

Similarly, we apply the convection boundary condition at the rightmost cell \((k = N_{cell})\)

\[ \lambda_0 \frac{\partial T_{0,N_{cell}}}{\partial x} \bigg|_{x=0} = h(T_{0,N_{cell}} - T_{amb}) \quad [28] \]

These equations thus establish the coupling between temperatures in adjacent cells.

In the single cell models, we must specify a current density boundary condition for the solid phase potentials \( \phi_{x,t} \) (Table I). In addition, a reference potential is specified as a Dirichlet condition to obtain a well-posed problem formulation. Similar relations must be specified for each cell in a stack model. For the stack model, the equality of terminal potentials \( \phi_{x,t} \) between the cells gives rise to \( N_{cell} - 1 \) unique coupling conditions for each cell terminal. Thus, at the negative electrode, we have

\[ \phi_{x,3,k,x=0} = \phi_{x,3,k+1,x=0} = 0 \quad [1 \leq k \leq N_{cell} - 1] \quad [29] \]

Where we specify a reference potential as above. Similarly, at the positive electrode, we have

\[ \phi_{x,1,k,x=0} = \phi_{x,1,k+1,x=0} = \phi_{x,1,k+2,x=0} \quad [1 \leq k \leq N_{cell} - 1] \quad [30] \]

Now, analogous to the single cell models, we must specify an overall current condition. For a parallel configuration, the current density \( i_{app,k} \) through cell \( k \) may be defined using the boundary conditions of Table I as

\[ i_{app,k} = -\sigma_{eff,1} \frac{\partial \phi_{x,1,k}}{\partial x} \bigg|_{x=0} \quad [31] \]

Now, the currents drawn from the individual layers must sum to the total stack value. This overall charge conservation is expressed in terms of the per-unit-area quantities as

\[ i_{app,stack} = \sum_{k=1}^{N_{cell}} i_{app,k} \quad [32] \]

Here, it is worth mentioning that for a parallel configuration, even during galvanostatic operation characterized by a constant total current \( i_{app,stack} \), inhomogeneities in the temperature profiles in individual cells may lead to variations in the individual \( i_{app,k} \) as a function of time. This model formulation predicts the instantaneous values of current densities and electrochemical variables simultaneously. This is in contrast to other approaches which first solve for electrochemical variables at a given time step, and then subsequently solve a circuit-level system of equations to compute current distributions.9,48

Equations 25–32 thus establish the additional boundary conditions and overall relations required to model an N-cell stack. This is in addition to the equation set of Table I for each individual cell. The equivalent Tanks-in-Series model can be generated by applying the standard volume-averaging and flux-approximation methodology to the equations of the individual cells (analogous to those in Table V).
as well as the additional constraints of Eqs. 25–32. The Tanks-in-Series modeling approach for the stack is illustrated in Fig. 4. The balance between internal conduction and external heat transfer can often be expressed in terms of the Biot Number, given by

\[ Bi = \frac{hR_t}{\lambda} \]  

Where the quantity \( R_t \) denotes the net thermal resistance of the cell stack given by

\[ R_t = \sum_{i=1}^{N_{\text{cal}}} \sum_{j=0}^{N_{\text{cal}}} \frac{I_{ij}}{\lambda_{ij}} \]  

A range of \( Bi \) numbers can thus be generated by varying both the value of \( h \) and the thermal resistance \( R_t \) by way of \( N_{\text{cell}} \). The Thermal Tank Model can then be evaluated under different operating current densities, with a view to establishing the limits of operation, which can help provide guidance a for the incorporation of the Stack Model in practical applications.

Figure 2. The extended Tanks-in-Series model for thermal effects. Additional variables introduced due to the consideration of thermal effects are highlighted in red. In particular, the average temperature \( T \) is introduced in each “Tank” by way of the heat conservation equations. The volume-averaged form of the equations also includes the interfacial heat fluxes \( \overline{q} \). The Thermal Tank Model also considers volume-averaged forms of the heat equations in two additional domains, namely the positive and negative electrode current collectors. The cell as a whole exchanges heat with the ambient surroundings via the external heat flux \( q_{\text{amb}} \).

Figure 3. Schematic of an \( N \)-cell stack. An instance of the p2D model (Fig. 1) is used to represent each individual sandwich (termed the “cell” in this work) in the stack. The \( N \) repeat units are connected in parallel and experience the same voltage \( V_{\text{cell}} \). The current densities from individual cells add up to the total value. The asymmetric temperature boundary conditions considered in this work are also indicated. The collector plate for the cell at the left extreme, is held at a constant temperature. The negative collector for the right extreme cell, on the other hand, is free to exchange heat with the surroundings. In the remainder of this document, the left cell is referred to as either the “leftmost” cell or the “hot” cell. The right extreme cell is similarly termed the “rightmost” or “cold cell.”
Figure 4. Computational schematic of the Tanks-in-Series representation of a cell stack. Individual layers are represented as Tanks-in-Series. The internal repeat unit includes one-half of each current collector, while the end cells consist of the entirety of the Cu collectors. This is illustrated by the relative sizes of the Cu collectors in the end and internal cells. The coordinate transformation strategy requires the temperature and flux relations highlighted in red, which are approximated using the Tanks-in-Series methodology.
Model and simulation details.—Single cell simulations.—Table II–IV list the parameter values and constitutive equations for a LiCoO₂ positive electrode and graphite negative electrode, taken from past work.21,25,46 Modified values for the high capacity case with electrolyte transport limitations may be found in Table VI. Electrolyte transport property correlations were adapted from the work of Valøen and Reimers.59 In the isothermal Tank Model, these properties are evaluated at the interfacial values of electrolyte concentration $c_{\text{p}}$. In extending these models to thermal effects, the electrolyte transport properties also depend on the interfacial value of temperature $T_c$. Other interfacial conditions that feature temperature, such as in Ref. 43, are also evaluated at the interfacial $T_c$. For the equations solved within the interior of a domain, relevant kinetic, transport and thermodynamic quantities were calculated at the average value $T$. The particle radii $R_c$, the current densities $i_{\text{app}}$, and the solid diffusion coefficients $D'_{\text{s}}$ were so chosen that the three-parameter model for solid phase transport is within the range of validity.50

Multi-cell stack simulations.—For the stack study, the electrode and electrolyte properties for the base case were used. The temperature boundary conditions at the ends of the stack for this study are depicted in Fig. 3. One end is maintained at a constant temperature (298 K), while the other extreme exchanges heat with the ambient surroundings by convection. An ambient temperature $T_{\text{amb}} = 263\,\text{K} \left( -10^\circ\text{C} \right)$ was used. Additionally, the cell was assumed to be at a uniform temperature of 298 K at the beginning of discharge. These conditions may be regarded as representing practical scenarios corresponding to a preheated battery operating under low-temperatures, such as for electric vehicles in cold weather, or electric aircraft applications.51 The study of the low-temperature performance of Li-ion batteries has significant practical value due to the increased capacity loss due to the enhanced thermodynamic favorability of lithium deposition reactions, and model-based studies and optimal charging strategies are actively explored.5,17 The variation of the ambient heat transfer coefficient $h$ in conjunction with ambient temperature $T_{\text{amb}}$ has been explored as a means to study the resulting deterioration in energy and power density.50 In addition, such a parametric study may have practical utility in guidance for preventing heat loss and insulation design for Li-ion cells under cold ambient conditions.52 The asymmetric boundary conditions impose a temperature gradient across the cell stack, which provides a relevant scenario to evaluate the Tanks-in-Series approach applied to multi-cell stacks.25,53 Table VII lists the parameter values used for the stack simulation studies.

Computational details.—The full electrochemical-thermal p2D model is used as the benchmark in evaluating the predictions of the Tanks-in-Series model. The p2D model was discretized and solved using coordinate transformation, model reformulation and orthogonal collocation techniques.55 The number of collocation points in each region were adjusted to achieve numerical convergence of discharge curves at different current densities up to 5 C, ultimately selecting $n = (2, 7, 3, 7, 2)$ Gauss–Legendre collocation points. This

<table>
<thead>
<tr>
<th>Table II. Additional constitutive equations for the isothermal p2D and Tank models.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$j_1 = k_i c_{\text{p}}/(c_i^{\text{max}} - c_i) \left( \exp \left( \frac{\alpha_{\text{p}} F j_0^i}{RT_i} \right) - \exp \left( \frac{-\alpha_{\text{p}} F j_0^i}{RT_i} \right) \right)$</td>
</tr>
<tr>
<td>$j_2 = k_i c_{\text{p}}/(c_i^{\text{max}} - c_i) \left( \exp \left( \frac{\alpha_{\text{p}} F j_0^i}{RT_i} \right) - \exp \left( \frac{-\alpha_{\text{p}} F j_0^i}{RT_i} \right) \right)$</td>
</tr>
<tr>
<td>$\alpha_{\text{p}}, i = \alpha_i(1 - \varepsilon_i - \varepsilon_j), i \in {1, 3}$</td>
</tr>
<tr>
<td>$a_i = \frac{k_i}{R_c}(1 - \varepsilon_i - \varepsilon_j), i \in {1, 2, 3}$</td>
</tr>
<tr>
<td>$[-4.656 + 88.669976p - 401.11904^4p + 3429090^6p - 462.47108^8p]$</td>
</tr>
<tr>
<td>$U_p = \frac{+33.43340^4p}{1.0 + 18.9330^2p - 79.5320^4p + 37.3110^6p - 73.0830^8p + 95.96^10p}$</td>
</tr>
<tr>
<td>$\theta_p = c_i^{\text{surf}}/c_i^{\text{max}}$</td>
</tr>
<tr>
<td>$U_0 = 0.7222 + 0.1387 \theta_0 + 0.02905 \theta_0^5 - 0.0172 \theta_0^8 + 0.0019 \theta_0^{12}$</td>
</tr>
<tr>
<td>$0.2808 \exp(0.90 - 15 \theta_0) - 0.7984 \exp(0.4465 \theta_0 - 0.4108)$</td>
</tr>
<tr>
<td>$\theta_0 = c_i^{\text{surf}}/c_i^{\text{max}}$</td>
</tr>
<tr>
<td>$1 + \left( \frac{\partial u_i}{\partial \theta} \right) = \nu(c_i, T) = 0.601 - 7.5894 \times 10^{-3} c_i^{0.5} + 3.1053 \times 10^{-3}(2.5236 - 0.00257)$, $i \in {1, 2, 3}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table III. Additional constitutive equations for the p2D and Tank thermal models.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{\text{app}, i} = F a_i j_0 \left[ \partial_i - \partial_j - U(c_i^{\text{surf}}) \right]$, $i \in {1, 3}$</td>
</tr>
<tr>
<td>$Q_{\text{app}, i} = F a_i j_0 \left[ \frac{\partial Q_i}{\partial T} \frac{c_i^{\text{surf}}}{c_i^{\text{surf}}} \right]$, $i \in {1, 3}$</td>
</tr>
<tr>
<td>$Q_{\text{dim}, i} = \alpha_{\text{eff}, i} \left( \frac{1}{l_i} \frac{\partial \theta_i}{\partial x} \right)^2 + \alpha_{\text{eff}, i} \left( \frac{1}{l_i} \frac{\partial \theta_i}{\partial x} \right)$</td>
</tr>
<tr>
<td>$\alpha_{\text{eff}, i} = 0.001 \times 10 \left[ \frac{1.431}{e^{3.25} - 0.0022} \right]$, $i \in {1, 2, 3}$</td>
</tr>
<tr>
<td>$\kappa(c_i) = 1 \times 10^{-4} \left[ -10.5 + 0.0740T - 6.96 \times 10^{-3}T_i^2 \right]$, $i \in {1, 2, 3}$</td>
</tr>
<tr>
<td>$\nu(c_i, T) = 0.601 - 7.5894 \times c_i^{0.5} + 3.1053 \times 10^{-3}$</td>
</tr>
<tr>
<td>$U_0(T_c, \theta_c) = U_0, c_i, \theta_c = 0.0527\nu, \theta_c$</td>
</tr>
<tr>
<td>$D(c_iT_c) = 0.0001 \times 10 \left[ \frac{1.431}{e^{3.25} - 0.0022} \right]$</td>
</tr>
<tr>
<td>$u_{\text{dis}, i} = \left( \frac{\partial u_{\text{dis}, i}}{\partial T} \right) \left[ \theta_{\text{ref}} \right]$, $i \in {1, 3}$</td>
</tr>
</tbody>
</table>

$0.199521039 - 0.928373822\theta_c^+$
$1.364550689000003 \theta_c^+ - 0.61544893999999 \theta_c^+$
$9.82431213599999 \theta_c^+$
$0.005269056 + 3.299265709 \theta_c - 91.79325792 \theta_c^+$
$1004.91110008 \theta_c - 581.2781271 \theta_c^+ + 19329.7549 \theta_c^+$
$37147.8947 \theta_c^+ - 38379.18127 \theta_c - 16515.05308 \theta_c^+$
$0.1001 \times 10^{-3} \left[ \frac{1.431}{e^{3.25} - 0.0022} \right]$, $i \in \{1, 3\}$
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
<th>Aluminum Current Collector</th>
<th>Positive Electrode</th>
<th>Separator</th>
<th>Negative Electrode</th>
<th>Copper Current Collector</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_i$</td>
<td>Porosity</td>
<td>0.385</td>
<td>0.724</td>
<td>0.485</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_{f,i}$</td>
<td>Electrode filler fraction</td>
<td>0.025</td>
<td></td>
<td>0.0326</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$b_i$</td>
<td>Brugemann tortuosity correction</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_i$</td>
<td>Particle surface area per unit volume</td>
<td>885000</td>
<td>723600</td>
<td></td>
<td></td>
<td></td>
<td>m$^2$ m$^{-3}$</td>
</tr>
<tr>
<td>$c_i^{a,\text{max}}$</td>
<td>Maximum particle phase concentration</td>
<td>51554</td>
<td>30555</td>
<td></td>
<td></td>
<td></td>
<td>mol m$^{-3}$</td>
</tr>
<tr>
<td>$c_i^{a,0}$</td>
<td>Initial particle phase concentration</td>
<td>25751</td>
<td>26128</td>
<td></td>
<td></td>
<td></td>
<td>mol m$^{-3}$</td>
</tr>
<tr>
<td>$c_{0}$</td>
<td>Initial electrolyte concentration</td>
<td>1000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>mol m$^{-3}$</td>
</tr>
<tr>
<td>$D_{\text{sp}}$</td>
<td>Solid phase diffusivity</td>
<td>1.0 $\times$ 10$^{-14}$</td>
<td>3.9 $\times$ 10$^{-14}$</td>
<td></td>
<td></td>
<td></td>
<td>m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>$k_i$</td>
<td>Electrode reaction rate constant</td>
<td>2.334 $\times$ 10$^{-11}$</td>
<td>5.031 $\times$ 10$^{-11}$</td>
<td></td>
<td></td>
<td></td>
<td>m$^{-2.5}$/mol$^{0.5}$ s$^{-1}$</td>
</tr>
<tr>
<td>$\alpha_{a,i}$</td>
<td>Electrode reaction anodic coefficient</td>
<td>0.5</td>
<td></td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_{c,i}$</td>
<td>Electrode reaction cathodic coefficient</td>
<td>0.5</td>
<td></td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$l_i$</td>
<td>Electrode thickness</td>
<td>10 $\times$ 10$^{-6}$</td>
<td>80 $\times$ 10$^{-6}$</td>
<td>25 $\times$ 10$^{-6}$</td>
<td>88 $\times$ 10$^{-6}$</td>
<td>10 $\times$ 10$^{-6}$</td>
<td>m</td>
</tr>
<tr>
<td>$R_i$</td>
<td>Characteristic particle radius</td>
<td>2 $\times$ 10$^{-6}$</td>
<td></td>
<td>2 $\times$ 10$^{-6}$</td>
<td></td>
<td></td>
<td>m</td>
</tr>
<tr>
<td>$i^0_{Li^+}$</td>
<td>Li$^+$ transference number</td>
<td>0.364</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\sigma_i$</td>
<td>Electronic conductivity</td>
<td>3.55 $\times$ 10$^7$</td>
<td></td>
<td>100</td>
<td>100</td>
<td></td>
<td>S m$^{-1}$</td>
</tr>
<tr>
<td>$T_{\text{ref}}$</td>
<td>Temperature</td>
<td></td>
<td></td>
<td></td>
<td>298.15</td>
<td></td>
<td>K</td>
</tr>
<tr>
<td>$i_{\text{app}}$</td>
<td>1 C Current Density</td>
<td></td>
<td></td>
<td></td>
<td>30</td>
<td></td>
<td>A m$^{-2}$</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Specific heat</td>
<td>897</td>
<td>700</td>
<td>700</td>
<td>700</td>
<td>385</td>
<td>J (kg K)$^{-1}$</td>
</tr>
<tr>
<td>$E_{a,sp}^{D_{\text{sp}}}$</td>
<td>Activation energy for temperature dependent solid phase diffusion</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>J mol$^{-1}$</td>
</tr>
<tr>
<td>$E_{a,i}^{D_{\text{sp}}}$</td>
<td>Activation energy for temperature dependent for kinetic rate constant</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>J mol$^{-1}$</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Thermal conductivity</td>
<td>237</td>
<td>2.1</td>
<td>0.16</td>
<td>1.7</td>
<td>401</td>
<td>W (m K)$^{-1}$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
<td>2700</td>
<td>2500</td>
<td>1100</td>
<td>2500</td>
<td>8940</td>
<td>Kg m$^{-3}$</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday’s constant</td>
<td></td>
<td></td>
<td>96487</td>
<td></td>
<td></td>
<td>Cmol</td>
</tr>
<tr>
<td>$R$</td>
<td>Gas constant</td>
<td></td>
<td></td>
<td>8.314</td>
<td></td>
<td></td>
<td>J (mol K)$^{-1}$</td>
</tr>
</tbody>
</table>
Table V. Governing Equations of the Thermal Tanks-in-Series Model for the porous domains.

<table>
<thead>
<tr>
<th>Positive Electrode (Region 1)</th>
<th>Separator (Region 2)</th>
<th>Negative Electrode (Region 3)</th>
</tr>
</thead>
</table>
| \[
\frac{d\tau_c}{dt} = \frac{3D(c_{12}, T_{12})(\tau_c - \tau_1) - \frac{h}{\epsilon_{12}} + \frac{l_2}{\epsilon_{22}}(1 - \tau_0^0)}{\phi_1} + \frac{L_{\text{app}}}{\phi_1}\]
| \[
\frac{d\tau}{dt} = \frac{-3D(c_{12}, T_{12})(\tau - \tau_1) + \frac{l_2}{\epsilon_{22}} + \frac{h}{\epsilon_{12}}}{\phi_1} + \frac{L_{\text{app}}}{\phi_1}\]
| \[
\frac{d\tau}{dt} = \frac{-3D(c_{23}, T_{23})(\tau - \tau_2) - \frac{l_3}{\epsilon_{33}} + \frac{h}{\epsilon_{23}}}{\phi_2} + \frac{L_{\text{app}}}{\phi_2}\]
| \[
\frac{d\tau_c}{dt} = \frac{3D(c_{12}, T_{12})(\tau_c - \tau_1)}{\phi_1} + \frac{L_{\text{app}}}{\phi_1}\]
| \[
\frac{d\tau}{dt} = \frac{-3D(c_{12}, T_{12})(\tau - \tau_1) + \frac{l_2}{\epsilon_{22}} + \frac{h}{\epsilon_{12}}}{\phi_1} + \frac{L_{\text{app}}}{\phi_1}\]
| \[
\frac{d\tau}{dt} = \frac{-3D(c_{23}, T_{23})(\tau - \tau_2) - \frac{l_3}{\epsilon_{33}} + \frac{h}{\epsilon_{23}}}{\phi_2} + \frac{L_{\text{app}}}{\phi_2}\]
| \[
\frac{d\tau_c}{dt} = \frac{1}{R_1} \frac{d}{dt} \left( 3D(c_{12}, T_{12})(\tau_c - \tau_1) \right) - \frac{h}{\epsilon_{12}} + \frac{l_2}{\epsilon_{22}}(1 - \tau_0^0) - \frac{L_{\text{app}}}{\phi_1}\]
| \[
\frac{d\tau}{dt} = \frac{1}{R_2} \frac{d}{dt} \left( -3D(c_{12}, T_{12})(\tau - \tau_1) \right) + \frac{L_{\text{app}}}{\phi_1}\]
| \[
\frac{d\tau}{dt} = \frac{1}{R_3} \frac{d}{dt} \left( -3D(c_{23}, T_{23})(\tau - \tau_2) \right) + \frac{L_{\text{app}}}{\phi_2}\]
| \[
\frac{d\tau_c}{dt} = \frac{1}{R_1} \frac{d}{dt} \left( 3D(c_{12}, T_{12})(\tau_c - \tau_1) \right) - \frac{h}{\epsilon_{12}} + \frac{l_2}{\epsilon_{22}}(1 - \tau_0^0) - \frac{L_{\text{app}}}{\phi_1}\]
| \[
\frac{d\tau}{dt} = \frac{1}{R_2} \frac{d}{dt} \left( -3D(c_{12}, T_{12})(\tau - \tau_1) \right) + \frac{L_{\text{app}}}{\phi_1}\]
| \[
\frac{d\tau}{dt} = \frac{1}{R_3} \frac{d}{dt} \left( -3D(c_{23}, T_{23})(\tau - \tau_2) \right) + \frac{L_{\text{app}}}{\phi_2}\]

where:

- \( \tau_c, \tau \) are the temperatures at the positive and negative electrodes, respectively.
- \( \tau_1, \tau_2, \tau_0^0 \) are the reference temperatures.
- \( D \) is the diffusivity.
- \( c \) is the concentration.
- \( R \) is the resistance.
- \( \phi \) is the porosity.
- \( L_{\text{app}} \) is the applied load.
discretization scheme was also used for the component cell models in the stack simulation studies.

The discretized equation systems were solved in time using IDA, an Implicit Differential-Algebraic solver in ANSI-standard C language under BSD license. IDA is an efficient solver for initial value problems (IVP) for systems of DAEs, which is part of the SUNDIALS (SUite of Nonlinear and DIfferential/ALgebraic equation Solvers) package. The absolute solver tolerance was set to \( \text{atol} = 10^{-8} \) and a relative tolerance of \( \text{rtol} = 10^{-7} \) was specified. All computations were performed on an Intel® Core™ i7-7700K processor with a clock speed of 4.2 GHz, 8 logical cores and 64 GB RAM.

**Results and Discussion**

**Single cell: base case.**—In this section, we evaluate the thermally augmented Tanks-in-Series model for representative cases of galvanostatic discharge. In particular, we consider two values of the convective heat transfer coefficient corresponding to practically relevant scenarios. In the first instance, we assume \( h = 0 \), implying a completely insulated cell operating adiabatically. The second case uses a relatively high \( h = 1000 \text{ W m}^{-2} \text{ K}^{-1} \) corresponding to fast convective heat transfer. These cases are termed as “adiabatic operation” and “fast heat transfer” respectively. A particular focus is the comparison of internal electrochemical variables and the accuracy of individual terms in the energy balances. The solid phase concentration (\( c_{ssur} \)) and potential variables (\( \phi_{i,j} \)) were compared and found to exhibit close agreement for the cases considered herein, and are not shown here.

**Discharge curves.**—Comparisons of the cell voltage from the thermally augmented Tanks-in-Series Model, hereafter termed the “Thermal Tank Model,” versus the full-order p2D model are depicted in Fig. 5. The agreement of the two models even for the relatively aggressive 5 C discharge rate is quite remarkable. Upon inspecting the instantaneous error profiles in Fig. 6, it is observed that the cell voltage error does not exceed 6 mV for adiabatic operation, and 15 mV for the fast heat transfer case. These metrics point to the competitiveness of the Tank Model in real-time frameworks and advanced BMS. As in the isothermal case, the errors arise primarily due to the approximate

![Figure 5](image-url)  
*Figure 5.* Comparisons of the Thermal Tank Model with the full-order p2D model for (a) adiabatic (b) fast external heat transfer scenarios.
nature of the flux equations, and the assumption of uniform reaction distribution in the electrodes.\textsuperscript{43}

The coupling of temperature with electrochemical transport phenomena helps understand the differences in errors for the two scenarios. In the adiabatic case, the heat generated during operation is expected to produce a rise in cell temperature, enhancing reaction kinetics and transport rates. Consequently, the polarization of the cell is reducing with time, dissipating gradients in both solid and liquid phases. This is in contrast to the fast heat transfer case, where the large external cooling rate results in near-isothermal operation for which the average cell polarization is higher. This explains the improved performance for the Tank Model for the adiabatic case.

Electrolyte phase variables.—As discussed in past work,\textsuperscript{43} the use of a diffusion length $\delta_{i,j} = \frac{1}{z}$ for electrolyte phase variables, corresponding to a parabolic spatial profile, substantially improves estimates of ohmic potential drop and concentration overpotential relative to the standard $\delta_{i,j} = \frac{1}{2}$ value. The agreement of the Tank Model is illustrated in, Fig. 7, which compares the concentration profiles for the two scenarios. For both the adiabatic and fast heat transfer cases, the maximum error in concentration is about 50 mol m$^{-3}$, corresponding to an error of less than 1% even for a 5 C discharge rate. In examining the concentration trends for the p2D model, we can notice pronounced fluctuations for the fast heat transfer case (Fig. 7b), which may be attributed to local variations in the reaction rate. Expectedly, the Tank Model predicts a rapid attainment of steady state at $t \sim 50$ s due to the uniform reaction assumption. The fluctuations for the adiabatic case are not as pronounced due to the rising temperature as the discharge progresses, which tends to enhance both kinetics and transport, homogenizing the reaction distributions (Fig. 7a). The effect of temperature is also reflected in the temporal variation of the concentration. While the concentrations rapidly attain a steady state during near-isothermal operation, during adiabatic operation the
concentrations first reach the same value on a comparable timescale (~50 s), but one then notices a gradual depletion of electrolyte in the negative electrode, accompanied by a corresponding increase in the positive electrode. These trends reflect the increase in diffusivities \( D(T) \) with temperature, which leads to a reduction in the concentration gradients required to sustain a given electrolyte flux.

Similar qualitative trends are seen for \( \phi_{li} \) as well (Fig. 8). The Tank Model exhibits close agreement for both average and

Figure 8. Representative electrolyte potential profiles at 5 C discharge for (a) adiabatic operation (b) fast heat transfer. As done elsewhere, the color convention of Fig. 1 is used.

Figure 9. Internal Temperature (left) and Surface Temperature profiles at Aluminum (peach) and Copper (purple) collectors at 5 C discharge rate for the (a) adiabatic and (b) fast heat transfer scenarios. The color convention of Fig. 1 is used.
interfacial values, with the maximum error not exceeding 3 mV for the adiabatic case, and 5 mV for the fast heat transfer scenario. The instantaneous fluctuations for $\Omega_{fl,1}$ in the negative electrode appear more pronounced than that in the positive electrode $\Omega_{fl,1}$, likely due to the faster kinetics in the negative electrode, and the more non-uniform reaction distribution that results. Expectedly, this is more discernible during near-isothermal operation, as in Fig. 8b.

The base case temperature boundary conditions, which define the heat fluxes at the collector surfaces, impose a near-symmetric temperature profile due to the comparable thicknesses and thermal conductivities of the electrodes and respective collector materials. In addition, the inherently low thermal resistance ensures near-uniform temperature for all operating conditions. While a simple lumped model is thus applicable for this case,\textsuperscript{40,42} these simulations represent the initial check for the accuracy of the Tank Model prior to use for stack simulations. The temperature trends for the two scenarios are illustrated in Fig. 9. As expected, the cell temperature exhibits a near-monotonic increase beyond $t = 50$ s during adiabatic operation, reaching approximately 356 K at $t \sim 700$ s. The Thermal Tank Model is able to ensure agreement with the p2D model even with the simple averaging procedure combined with the naïve approximations for “thermal diffusion length.” A caveat in interpreting the adiabatic results is that the transport property correlations used in this work are only valid up to a temperature of 333 K, beyond which they are extrapolated.\textsuperscript{12} However, the same property correlations are used in comparing both models, so the evaluation of the Thermal Tank Model holds. In contrast to the adiabatic case, using a value $h = 1000$ W m$^{-2}$ K$^{-1}$ results in a near-constant temperature throughout the cell, as depicted in Fig. 9b, indicating the establishment of a steady-state value of temperature corresponding to the balance between the net internal heat generation rate and the rate of convective heat dissipation. For this case, it is interesting also to note an extremely small but finite internal temperature gradient in the cell. From Fig. 9b, it can be seen that the temperature at the surface of the Al collector (peach) is marginally higher ($\sim 3$ mK) compared to the Cu collector (purple). This may be attributed to variations in the local heat generation rates and the conduction resistances of the materials. In practice, degradation and thermal decomposition reactions of the electrodes, electrolyte and other components, are likely to be triggered above a temperature threshold, leading to accelerated capacity degradation and potential thermal runaway. These reactions are not considered in our models, but the temperature prediction from the Thermal Tank Model could be used as rough threshold guidelines by a BMS to define safe operating limits for a given battery. Further, the Thermal Tank Model represents a simplified framework for the integration of explicit models for delusory side reactions.

**Thermal variables.**—The results thus far indicate the ability of the approximate Thermal Tank Model, with its substantially reduced computational footprint, to predict the temperature variation of a single Li-ion cell under practically relevant conditions. Increasing the value of the heat transfer coefficients tends to increase the magnitude of temperature gradients within the cell by altering the balance between conduction and convection resistances. Typically, this is expressed in the form of a dimensionless group such as the Biot number $(Bi)$.\textsuperscript{12} For the parameters considered for a single cell, the value of $Bi$ number is low enough to ensure the validity of lumped thermal approximations.\textsuperscript{40,42} For a cell consisting of several layers of these Li-ion “sandwiches,” the length scales for conduction and thus the corresponding resistances are expected to be substantially higher, leading to higher values of $Bi$ for a given value of $h$.

The limit of applicability of the Tanks-in-Series methodology is tackled in subsequent sections studying the performance of the Thermal Tank Model over a range of $Bi$ values.

While the agreement in temperature profiles indicates the validity of the Thermal Tank Model approximation for the heat balance, it is important to examine its ability to predict individual terms therein, the relative contributions of which change according to cell parameters and operating conditions. This is especially true for the various heat generation rates,\textsuperscript{44} errors in prediction of which can produce erroneous temperature predictions, potentially compromising the ability of BMS and TMS to ensure safe operation in practical scenarios. Figure 10 illustrates the comparisons of reversible and irreversible heat generation rates in the positive electrode. It can be seen that the Thermal Tank Model matches closely with the average value from the p2D model. The local generation rates at the extremities of the electrode domain are also shown to indicate the spatial distribution. It is interesting to note that the reversible heating rate exhibits only slight variation across the electrode thickness (Figs. 10a and 10b). Greater spatial non-uniformity (between $\sim 200$–400 s) is obtained for the fast heat transfer case, consistent with the more non-uniform reaction distribution. Additionally, $Q_{rev,1}$ is initially higher near the separator-interface, but the maximum shifts towards the current collector as the active material saturates. $Q_{rev,1}$ Values are comparable for the two cases, which indicates the effect of local pore-wall flux and the entropic coefficient $\frac{\partial (\Delta G_{298})}{\partial t}$ (Eq. 20). A noteworthy feature is the relatively large negative value of $Q_{rev,1}$ at short times ($t \sim 50$ s), which has implications for the resulting cell temperature trends, and will be discussed presently.

Figures 10c and 10d compare the variation of the irreversible electrochemical heat $Q_{rev,1}$. The agreement of the Thermal Tank Model approximation with the averages obtained from the p2D model is quite noteworthy, with very marginal errors of $\sim 1\%$ observed for the fast heat transfer case towards the end of discharge. This may be related to the accuracy in predicting the average potential quantities, and thus the reaction overpotentials. The spike in $Q_{rev,1}$ at the collector towards the end of discharge may be explained by Eq. 19, likely due to the sharp increase in overpotential towards the end of discharge due to local exhaustion of active material, in addition to the large local reaction rate at the collector. Figure 10c indicates a slightly lower generation than the fast heat transfer case, and this may be due to the lower average polarization during adiabatic operation. This difference is more pronounced towards the end of the discharge process at $t \sim 500$ s, particularly at the current collector. Greater non-uniformity in $Q_{rev,1}$ is observed for the fast heat transfer case, in line with expectations. The marginal error observed for the fast heat transfer case may thus be attributed to the limitations of the Tank average expression.

The same set of variables are now plotted for the negative electrode in Fig. 11. Here too, we observe the close agreement of the Thermal Tank average with the p2D model. In the profiles for $Q_{rev,3}$, one notices greater non-uniformities in Fig. 11b compared to the adiabatic case, as expected for less uniform reaction distributions. The assumptions of uniform pore-wall flux by the Thermal Tank Model also result in certain fluctuations in the Thermal Tank average $Q_{rev,3}$ about the p2D average after the initial constant portion at $t \sim 300$ s. The overall trends are in line with the $\frac{\partial (\Delta G_{298})}{\partial t}$ profile for the graphite electrode. The higher value of $T_i$ for the adiabatic case may explain the marginally higher value of $Q_{rev,3}$ towards the end of discharge. As with the positive electrode, there is a substantial “endothermic” portion characterized by negative values of $Q_{rev,3}$, though the magnitude of $Q_{rev,3}$ is substantially lower than the corresponding $Q_{rev,1}$.

The agreement of the irreversible heating averages in Figs. 11c and 11d may be related to the accuracies in predicting the average potential quantities. The spike in the heat generation rate at the end of discharge may be related to the exhaustion of Li in the negative electrode particles, and the corresponding increase in polarization. The reaction rate non-uniformity may explain the differences in heat generation rates, especially at the collectors at the end of discharge in Fig. 11d. Of note, while both $Q_{rev,3}$ and $Q_{rev,3}$ initially exhibit significant spatial non-uniformities, beyond $t \sim 600$ s, the local values rapidly converge to the average value given by $\frac{\sum_{n} J_n}{F_{rev}}$. This may be explained by the pore-wall flux profiles $j_3$ in Fig. 9b of Ref. 43 As
the fraction of Li in the graphite particle (\(c_{ss \ u r f}^{3,m a x} \)) reduces during discharge, below a certain degree of lithiation the equilibrium potential exhibits a sharp and monotonic variation coinciding with the presence of a single intercalant phase. This in turn rapidly homogenizes the reaction distribution as argued in past work, which is manifested in the electrochemical heat generation terms.

The ohmic heat generation terms \(Q_{ohmic,i} \) in the electrodes are now depicted in Fig. 12. Notably, the local heat generation at the current collector interface is at least an order of magnitude lower than at the electrode-separator interface. An additional feature is the gradually reducing instantaneous \(Q_{ohmic,i} \) with discharge time during adiabatic operation, as observed in Figs. 12a and 12c. For both scenarios, the Thermal Tank Model approximations of Eqs. A·8 and A·9 is able to achieve substantial agreement with the p2D model. As with other volumetric terms, we expect the chief source of qualitative differences to be the non-uniformities in the reaction distribution, which in turn result in oscillations in electrochemical variables, as observed in Figs. 8b and 7b. For all cases, discernible fluctuations may be observed for the p2D average \(\overline{Q_{ohmic,i}} \) at approximately \(t \sim 400 \text{ s} \) in the negative electrode, and towards the end of discharge in the positive electrode (\(t \sim 700 \text{ s} \)). These features closely track similar fluctuations observed in the profiles for both \(c_{i} \) and \(v_{L,i} \). Oscillations are observed even for adiabatic operation in the negative electrode, and this may again be attributed to the less uniform pore-wall flux distribution on account of the inherently faster kinetics and flatter equilibrium potential curves vis-à-vis the positive electrode.

The large difference in \(Q_{ohmic,i} \) at the separator and current collector interfaces may be explained in terms of Eq. A·1. For most practical batteries, the electronic conductivity of the electrodes is about an order of magnitude higher than the ionic conductivity of the electrolyte. This means that the ionic current contribution to the ohmic heat generation is higher than that due to electronic resistances. At the electrode-separator interfaces, the total current density is carried in the form of ionic current based on the boundary conditions (Tables V and I), leading to a maximum in \(Q_{ohmic,i} \) given the gradients in \(v_{L,i} \) required to drive the current. The situation is reversed at the current collector, where the ionic current is zero, and the entire applied current \(i_{app} \) exists in the form of electrons. The reduced electronic resistance vis-à-vis the ionic term means that substantially smaller gradients of \(c_{i} \) are required to sustain the applied current \(i_{app} \) at the current collector. Indeed, we neglect this contribution in the Thermal Tank Model approximations of Eqs. A·8–A·10.

In Figs. 12a and 12c for the adiabatic case, the instantaneous average \(\overline{Q_{ohmic,i}} \) first attains a maximum, and then gradually reduces with time. These trends mirror those for the electrolyte phase variables \(c_{i} \) and \(v_{L,i} \). In contrast, for the fast heat transfer case, \(Q_{ohmic,i} \) rapidly reaches a near-constant maximum value at relatively short times. The discussion on the electrolyte phase variables indicates that these trends are expected. For adiabatic operation, the uniform cell temperature, which increases with time, gradually equalizes the reaction distribution and dissipates the spatial gradients of the electrolyte variables. The reducing concentration and potential gradients in turn lead to a reduction in instantaneous \(\overline{Q_{ohmic,i}} \). The downward trend during adiabatic operation and the near-constant generation rate for the near-isothermal
scenario is also observed for the separator $Q_{\text{ohmic},2}$ (Fig. 13). However, the spatial distribution of heats is nearly uniform since the current density is carried as ions throughout the domain. The relatively smaller thickness of the domain also means that it is easier to match ohmic heating rates compared to the electrodes, where the gradients are higher in magnitude. It is also worth noting that, unlike the approximations for the electrodes, Eq. A·44 is an exact relation obtained by a rigorous volume-averaging. Therefore the accuracy of the $Q_{\text{ohmic},2}$ by the Thermal Tank Model is directly dependent on the accuracy of the predictions for $\theta_{li}$. For the parameters considered here, the polarizations in the electrolyte phase are sufficiently captured by the Tank Model approximations. However, significant spatial gradients arise can introduce substantial mismatches in predictions of electrolyte potential, with attendant implications for the accuracy of cell-level voltage and temperature predictions. The accuracy of $Q_{\text{ohmic},1}$ and $Q_{\text{ohmic},3}$ is limited by errors in not just $\theta_{li}$, but also mismatches in reaction overpotential due to the uniform pore-wall flux assumption.

To provide an sense of the relative magnitudes of the various heat generation rates, Fig. 14 plots the values of $Q_{\text{rev},i}$, $Q_{\text{irrev},i}$ and $Q_{\text{ohmic},i}$ on the same scale. Upon inspection of the figure, it can be seen that the endothermic $Q_{\text{rev},i}$ for both electrodes dominate the net heat generation rate at short times till about $t \sim 150$ s. The magnitude of $Q_{\text{rev},1}$, for instance, is $\sim 200,000$ W m$^{-3}$, about four times the values of other terms. This explains the slight initial fall in cell temperatures for both cases, as noted in Fig. 9. Beyond $t \sim 200$ s, $Q_{\text{rev},1}$ far dominates the other sources for the cell parameters and operating conditions considered here. It is worth noting that $Q_{\text{rev},1}$ is higher for the adiabatic case than the fast heat transfer case, where the cell is nearly isothermal. The increase in temperature increases the instantaneous generation rate due to its dependence on temperature via Eq. 20. This also explains the increased generation rate for the negative electrode as well, towards the end of discharge when the $\frac{\partial \theta_{li}(x,y,t)}{\partial t}$ profile for graphite begins to increase. The increase of $Q_{\text{rev},1}$ towards the end of discharge is consistent with the sudden spike in cell polarization due to the saturation of the solid particles in the positive electrode, and the depletion of Li in the negative electrode particles. The heat generation trends reported herein are consistent with predictions from other workers. Figure 14 indicates that while the relative contribution of $Q_{\text{ohmic},1}$ may be only a fraction of the total generation rate, the instantaneous generation rates are comparable over certain portions of discharge. Ohmic heating plays an important role up to $t \sim 50$ s. This indicates that this contribution may be important during short timescales, especially in scenarios of dynamic variations in applied current, as seen in other works. While the total magnitude of these rates is much lower than electrochemical heats, it could also become significant in high current-density regimes or cells in which significant electrolyte phase limitations can exist, such as ultra-thick electrodes. Having a simplified yet physically meaningful expression for the various contributions is thus more valuable than the use of empirical expressions given the clear connection to battery electrochemistry, information of which can be incorporated into algorithms of BMS and TMS. A detailed analysis is required to quantify the relative contribution of the different heat generation terms under a range of parameter combinations and operating conditions, while also quantifying the resulting accuracy of the Thermal Tank Model.
Single cell: electrolyte phase limitations.—Representative results for the thick electrode case are shown in Fig. 15. The reduced accuracy of the Tank Model flux approximations for the thick electrodes is evidenced in the concentration profiles of Fig. 15a, with resulting errors in concentration overpotentials leading to increased Root Mean Square Errors (RMSE). For the adiabatic case with \( h = 0 \), the concentration profiles gradually converge as the temperature increases with discharge. Thus, even for such transport-limited situations, internal heating serves to reduce transport resistances, improving the validity of the approximations. For the fast heat transfer case, the Thermal Tank Model greatly overpredicts the electrolyte depletion in the positive electrode and consequent termination of discharge at \( t \sim 300 \) s. This suggests a mismatch in estimating the liquid phase gradients in the thick electrodes, since the average electrolyte transport resistances are substantially higher for this near-isothermal case. Despite this limitation, the RMSE values are \(<30\) mV for adiabatic operation up to an aggressive 150 A m\(^{-2}\). For \( h = 1000\) W m\(^{-2}\) K\(^{-1}\), acceptable errors \(<20\) mV are achieved up to 60 A m\(^{-2}\), which is still a high operating current for the high-energy cell parameters considered herein. This study illustrates the ability of the Thermal Tank Model to match the full model over a wide range of parameters. The error comparisons of Fig. 15b suggests a threshold current density at which severe electrolyte phase resistances cause a breakdown of the Tank Model approximations, and the resulting mismatch in concentration overpotentials sharply increases voltage errors. This effect is further discussed in subsequent sections. Of note, while the simulated temperatures are higher than the threshold of validity of transport property correlations, identical expressions are used in evaluating both models.

Multi-cell stacks.—The following subsections thus detail the comparison of the Stack Thermal Tank Model (sTTM) with the Stack p2D model (hereafter termed the sp2D model), with a particular focus on cell voltage, temperature, and current distribution predictions. The focus of this study is to examine the effect of effective thermal resistances and discharge rates on the accuracy of the Thermal Tank Model for a practical case of a multi-cell stack. An important aspect of the study is evaluating the performance of the Thermal Tank Model as the effective length scale for thermal transport increases with the number of cells.

Representative discharge curves.—Figure 16 depicts representative discharge curves for a 10-cell stack for two representative values of the Biot number. In this study, the Bi numbers are varied through different values of the ambient heat-transfer coefficient \( h \). The agreement of the sTTM for \( Bi = 0.01 \) is remarkable, even up to an 8 C discharge rate. In contrast, the sTTM exhibits substantial error beyond 1 C for the high Bi case. This indicates the limitation of the Tank Model flux approximations, especially beyond 4 C discharge rates. While the sTTM is able to predict the increased polarization at higher rates, the full model predicts a premature termination of discharge relative to the Tank Model. The end-of-discharge discrepancy is likely due to the prediction of a sudden drop in \( V_{\text{cell}} \) corresponding to a sharp increase in polarization. While this feature is captured by both models, the much larger DAE system size of the sp2D model leads to a numerical singularity at \( t \sim 50 \) s for the 8 C curve in Fig. 16b due to increased numerical stiffness relative to the sTTM, which reaches a singularity at marginally longer times (\( t \sim 80 \) s for the same case). The premature termination

Figure 12. Representative contributions to the ohmic heating terms in the electrodes at 5 C discharge for positive electrode (a) and (b), and negative electrode (c) and (d) for the two respective cases.
of discharge under aggressive diffusion-limited operating conditions has been observed in other works.\textsuperscript{5,59,60}

An examination of the electrochemical and temperature profiles is now conducted in order to determine the chief source of error. In particular, the temperature drop across the cell is likely to be substantially higher for $Bi = 10$ than $Bi = 0.01$. The coupling between temperature and the electrochemical variables will increase errors due to both the thermal and electrochemical approximations. An additional source of error is the three-parameter model used for simplifying solid-phase diffusion, which may introduce numerical errors in solid phase concentrations at high discharge rates and low temperatures, affecting the estimation of reaction overpotentials. However, this error was determined to be negligible for the cases considered in this study.

**Representative concentration and temperature profiles.**—Figure 17 depicts representative electrolyte concentration profiles as a function of distance at $t = 300$ s. A nearly symmetric profile is observed for the $Bi = 0$ case. In addition, there is close agreement between the sp2D average value and those predicted by the sTTM. Beginning from the leftmost porous domain in Fig. 1, each “point” may be mapped to the corresponding porous domain (ignoring the collectors, where the equations for $c_1$ are not applicable). Thus the first average point corresponds to the negative electrode $\Sigma c_i$ for the leftmost cell, followed by the separator $\Sigma c_i$, and so on. The near-symmetric concentration profile suggests a near-uniform temperature distribution across the cell stack, consistent with zero heat transfer from the cold end, and thus the stack temperature rapidly attains a uniform 298 K. The concentration drop across each cell is nearly equal, suggesting near-identical polarization in each cell. The error in average concentration is marginally higher in the positive electrode domain relative to the negative electrode and separator domains. The profiles of Fig. 17b represent an interesting contrast, on the other hand. It can be seen that, for high $Bi = 10$, the concentration drop across each cell increases in magnitude as we move right from the leftmost cell which is held at a constant temperature. The increasing concentration drop as we approach the “cold” end, suggests a progressive decrease in cell temperature with $x$. The consequent decrease in diffusion coefficient leads to the increased concentration gradients required to drive the electrolyte flux. It is also expected that the non-uniform temperature distribution across the stack will lead to non-uniformities in the effective cell resistances, and thus in the current distribution across the individual cells, which will also influence concentration profiles. Additionally, the positive electrolyte concentration $\Sigma c_i$ in the leftmost cell is $\sim 500$ mol m$^{-3}$ but reduces to $< 100$ mol m$^{-3}$ at the rightmost cells. This severe electrolyte depletion in the “colder” cells is then the reason for the termination of the 4 C discharge observed in Fig. 16b. Of particular relevance, the agreement with the sTTM and the sp2D averages is close near $x = 0$, but the errors in $\Sigma c_i$ increase as we move towards the colder end. The mismatch is most pronounced towards the rightmost cells, reaching a maximum of $\sim 200$ mol m$^{-3}$, which is a substantial 20\% of the initial concentration $c_0$. There are two factors that can potentially contribute to this error—the limitations of the Tank Model flux approximations in capturing the large $\Delta c$ at low $T$, and errors in prediction of the $T_i$ themselves, which affects the estimates of transport properties such diffusion coefficients $D(\Sigma c, T_i)$.

Temperature profiles for the two cases are illustrated in Fig. 18. From Fig. 18a, for $Bi = 0.01$, the temperature decreases across the cell-stack, leading to a total $\Delta T \sim 20$ K. The sTTM predictions match closely with that of the sp2D model, indicating the accuracy of the Thermal Tank Model approximations for heat flux and generation rates. The difference between the cold end and the ambient temperatures ($T_{amb} = 263$ K) corresponds to the value of the convective flux for the given heat transfer coefficient. For the large $Bi = 10$, the temperature drop is expectedly higher, as seen in Fig. 18b. The average $T_i$ reduces from 298 K at the hot end to nearly 267 K at the cold end, corresponding to a temperature drop of approximately 3 K per cell. The substantial temperature inhomogeneity thus explains the trends in concentration gradients discussed previously. The value of ambient heat transfer coefficient $h$ is 1000-fold higher than the $Bi = 0.01$ case, which explains the smaller temperature difference required sustain the convective flux at the right surface. The marginally higher temperature drop across the separator domains is consistent with its significantly higher thermal resistance relative to the more conductive electrode and collector domains. It is also worth noting that even at 4 C, for the high $Bi$ case the heat dissipation rate by convection from the cold end, combined with the constant temperature boundary condition at the leftmost end, dominates the internal heat generation rates, giving rise to the observed temperature levels.

Even for a high $Bi = 10$, where the temperature drop is clearly discernible, the sTTM predictions of $T_i$ match closely with the full sp2D model, indicating the suitability of the Thermal Tank Model to capture the temperature variations within a given domain, even for a 4 C discharge rate. It must be noted that these trends may change for different parameter combinations. For example, for the same $Bi$ value, the performance of the sTTM may deteriorate for a cell-stack in which the individual cells have much thicker electrodes. However, this is more likely to be to the inherently higher cell polarizations.
that the Tank Model is unable to account for, as discussed previously. For an expected "baseline error" based on the parameters of the single cell, it is possible to determine the upper limit of $Bi$ based on acceptable error metrics of stack-level $V_{cell}$ and temperature predictions, which can help define performance limits of BMS and TMS.

The temperature profiles in Fig. 18b suggest that the errors in the electrochemical variables, which contribute to the errors in $V_{cell}$ through the estimates of various polarization contributions, do not significantly affect the predictions of the heat generation rates and fluxes. These trends are further emphasized through the error profiles in Fig. 19, which compares errors in $\tau_f$ and $T_f$ for the two cases. For
Figure 16. Representative discharge curves for 10-cell stack at representative values of low and high Biot numbers, namely (a) $Bi = 0.01$ (b) $Bi = 10$.

Figure 17. Representative spatial profiles of electrolyte concentration for a 10-cell stack and 4 C discharge at a typical $t = 300$ s, for two cases of (a) $Bi = 0.01$ and (b) $Bi = 10$ showing the x-profile from the sp2D model (dashes), the sp2D average (circles), and the Tank Average (crosses). The vertical dotted lines are intended to demarcate the individual cells.

Figure 18. Spatial profiles of Temperature for a 10-cell stack and 4 C discharge at a typical $t = 300$ s, for two cases of (a) $Bi = 0.01$ and (b) $Bi = 10$. The averages across each porous domain are plotted at the corresponding midpoint for convenience. As with the concentration profiles, vertical dotted lines are used to denote the boundaries between adjacent cells. Unlike $\tau$, $T$ is modeled in the collector domains as well, and is indicated accordingly.
Both the $Bi = 0.01$ and $Bi = 10$ cases, the maximum error in $T_i$ does not exceed 0.12 K. It is also noteworthy that the maximum error in $T_i$ is marginally higher for lower $Bi$ than the less homogenous $Bi = 10$ case. In addition, the error in $T_i$ is highest towards the center of the cell stack ($x \sim 1300 \mu m$) for the $Bi = 10$ case, as opposed to Fig. 19a, where the error maximum is attained at the right extreme. The profiles in Fig. 19b for $Bi = 0.01$ indicate $\tau$ errors in the 5–25 mol m$^{-3}$ range, with expectedly lower errors in the separator domains. The error levels in the respective domains are nearly constant across the stack in the $x$-direction. This is consistent with typical temperature levels and variations across the stack. The minimum temperature in the stack is $\sim 281$ K, which appears to be high enough for the Tank Model approximations to capture the liquid phase and kinetic polarizations. In Figs. 17b, we can observe the increasing concentration gradient as temperatures decrease along the $x$-direction. For the fast external heat transfer case of $Bi = 10$, the performance of the overall stack is essentially limited by the increased polarization in the low temperature cells due to electrolyte depletion. The difference between the tank and sp2D model performance is also clear, sometimes as high as two-fold, as seen in the error plots of Fig. 19. The errors in $\tau$ in the respective domains can be seen to increase away from the “hot” end. The Tank Model, by its very nature reduces in accuracy as the liquid phase non-uniformities increase in magnitude, as is the case at lower temperatures characterized by slower kinetics and transport. The study of these profiles thus indicates that, for the given set of cell parameters, the error in $V_{cell}$ due to non-uniform temperature profile is not due to errors in predictions of $T_i$ by the sTTM. It is primarily due to the interplay between temperature and other electrochemical variables. Inhomogeneous temperature distributions and low temperatures produce kinetic polarizations and liquid phase gradients that are not adequately captured by the Tank Model approximations, even though the temperatures themselves are well-approximated.

The temperature-dependent limitations may be circumvented by refining the Tank Model approximations via a temperature-dependent diffusion length, i.e. $\delta_{ij}(T_i)$ may be replaced by $\delta_{ij}(T_i)$. This is reasonable since the characteristic boundary layers are a function of the temperature-dependent transport properties. The sTTM can be parameterized using experimental data to determine these adjustable values. During real-time operation, a BMS may be able to vary these diffusion lengths for each individual cell based on predictions or measurements of instantaneous temperatures, refining the flux approximations on the fly, thus improving predictions of $V_{cell}$.

Effect of $Bi$.—Given the dependence of the accuracy of the sTTM on the effective Biot number and operating conditions, it is worthwhile to determine approximate performance limits for the sTTM as a means of providing guidance for model selection. This can be done by comparing error metrics with respect to the sp2D model for simulations over a range of relevant parameter
combinations. For example, we can vary the operating current density in conjunction with parameters pertaining to the external heat transfer conditions, such as \( h \), \( T_{amb} \), and the terminal temperature boundary conditions (Fig. 3). We can also test the accuracy of the sTTM for \( V_{cell} \) as a function of \( N_{cell} \). To illustrate such a “performance chart,” we vary the \( N_{cell} \), the effective current density \( i_{app,stack} \), and the ambient heat transfer coefficient \( h \). Errors from these simulation runs can then be plotted as a function of the calculated values of \( Bi \) and C-rate for each case. The results from one such study are illustrated in Fig. 20, which shows the Root Mean Square Error (RMSE) for the sTTM against the benchmark sp2D model. Inspection of Fig. 20 reveals an interesting trend of RMSE as a function of \( Bi \). For a given C-rate, the RMSE remains almost constant for a large range of \( Bi \). However, beyond a certain threshold value, there is a sharp increase of nearly an order of magnitude, which indicates the increasing effect due to the polarization in the “weaker” cells, which are at lower temperature. Temperature gradients in turn result in non-uniform current density distributions across individual cells. The temperature variation also affects the accuracy of the other electrochemical variables due to higher overall polarization and the non-linear dependence of temperature on transport and kinetic properties, which is only partially captured by the approximations of the Tank Model. Expectedly, this threshold \( Bi \) reduces by approximately an order of magnitude with increasing discharge rate, from \( Bi \sim 1 \) for 4 C to \( Bi \sim 0.1 \) at 8 C. The horizontal dotted line indicates the 10 mV threshold, which is typically the acceptable error in onboard estimation, optimization and control applications. It can be seen that the RMSE for the sTTM is below this value up to 4 C and \( Bi \sim 0.7 \). This indicates a wide range of applicability of the Tank Model, even for the asymmetric temperature boundary conditions considered herein. The region of applicability can be further extended if we relax the acceptable error, for instance if a threshold of 20 mV will also envelope certain \( Bi \) values at 8 C. We would also expect the specific values of errors and error thresholds to change with the temperature boundary conditions and cell parameters, although the qualitative trend is expected to be identical. Varying the cell parameters will alter the “baseline error” due to the electrochemical variables at a given C-rate, an estimate of which can be obtained by extrapolating the curves in Fig. 20 towards

\[
\text{Figure 20. Comparison of Root Mean Square Error (RMSE) as a function of Biot Number at different discharge rate. For simulations which terminated prematurely, the discharge curves were extrapolated to the cutoff voltage (2.8 V) to simplify error calculation.}
\]

\[
\text{Figure 21. Representative current density split through the extremum cells in a 10-cell stack for a 2 C discharge, for two cases of (a) \( Bi = 0.01 \) and (b) \( Bi = 10 \).}
\]

\[
\text{\( Bi \to 0 \). This value may also be obtained by simulating the insulated cold end case where \( h = 0 \), as was shown in previous sections. For the range of \( Bi \) considered in this study (10^{-4} \sim 10), we do not observe the sharp increase in RMSE for the 1 C case due to the cell parameters considered herein. However, the RMSE for an aggressive \( Bi = 1000 \) case was found to be \( \sim 800 \text{ mV} \), pointing to a threshold at an intermediate value of \( Bi \). An important caveat in interpreting this result is that the numerical convergence for the sp2D models may be compromised beyond \( Bi > 10 \), but the qualitative trend still holds. In addition, the three-parameter model for the solid phase may also require reexamination at lower temperatures, as discussed previously, and efficient higher-order methods from our group may be explored for this and other aggressive cases.} \]

\[
\text{Using the sTTM for cell-level monitoring.—We can now use the results of the stack simulations to illustrate the ability of the Tanks-in-Series approach to predict current distributions and the SoCs of individual cells. Importantly, we compare the sTTM against the full sp2D models by examining the time-dependent profiles for the individual layers in the stack. Figure 21 represents current density profiles through the two end cells at 2 C. The current density split is illustrated by plotting the ratio of the actual current density to the nominal value, \( \beta_k = \frac{i_{appk}}{i_{app,avg}} \).}
\]
for cell $k$. Given the boundary conditions used in the previous study, the end cells also represent temperature extrema, and thus may reasonably be expected to have different effective dynamic resistances. Useful insight into the current distribution may thus be obtained by examining the currents and SoCs in these cells. Figure 21a depicts these profiles for $Bi = 0.01$. The $\beta$ profiles for the two cells are nearly symmetric about the y-axis. Additionally, the variations in instantaneous current density are negligible, with the maximum deviation about the average only $\sim 0.002$. The overall current distribution is relatively uniform. The increase in the current density for the hot cell at short times is consistent with its higher temperature (298 K). In contrast, the effective resistance of the “colder” cell increases as its temperature reduces to its pseudo steady-state value. Thereafter, $\beta$ vary based on the instantaneous cell resistances. The symmetric $\beta$ profiles indicate nearly equal cell utilization over the entire discharge process (which can also be seen by examining the area under the respective curves, a measure of the total charge drawn). The close agreement of the sTTM in predicting these trends is expected given the relatively uniform temperature profiles and suggests its ability in accurately predicting the current distributions in large multi-cell configurations. The observed $\beta$ profiles are in qualitative agreement with experimental data from similar studies on parallel configurations of cylindrical cells.\(^{18}\)

For the $Bi = 10$ case, Fig. 21b indicates substantial non-uniformity in the current density distribution, likely due to the nearly 30 K temperature difference. As with the previous case, the sharp temperature drop in the cold cell (298 K at $t = 0$ to 267 K) increases its instantaneous resistance, reducing the amount of current drawn (it must be remembered that the cells are connected in parallel, and thus experience the same $V_{cell}$). In contrast, $\beta$ for the “hot” cell sharply increases to over 20% of the average value. This indicates an overloading of the higher temperature cells because of their lower resistance, especially during the initial portions of the discharge. The “cold” cell remains underutilized until $t \sim 1200$ s due to its higher overall resistance arising out of slower kinetics and transport processes. Around $t \sim 1200$ s, the decrease in $\beta$ for the “hot” cell is accompanied by a concomitant increase for the colder cell. The decrease is likely due to the increased kinetic overpotential in the electrodes associated with the saturation and depletion of active material in the overloaded cell. This increases the cell resistance above that of the colder cells, causing the currents to now be drawn predominantly from the latter. This “overloading” of the colder cells, in order to maintain the total current density $\text{Lapp,stack}$, substantially increases the polarization. From the previous section, this is chiefly concentration polarization due to diffusion limitations. Slow electrolyte diffusion leads to electrolyte depletion, which explains the sudden drop in $V_{cell}$ due to the consequent spike in concentration overpotential. In Fig. 21b, this is reflected in the sudden decrease in $\beta$ as the rightmost cell is no longer able to sustain the same level of current.

Around $t \sim 800$ s, the predicted value of $\beta$ predicted by the sTTM prediction also starts to diverge from the benchmark sp2D model. This is consistent with the errors observed in $\tau_i$, due to the inability of the Tank Model to capture the increasing concentration gradients as the current density drawn from the cold cell starts to increase. As observed previously, the sTTM substantially overpredicts the electrolyte concentration in the positive electrode, thereby underestimating the concentration overpotential, and thus the effective cell resistance. This causes the mismatch to increase as the discharge progresses, since the sTTM predicts that the cell can now sustain even higher currents, and the sTTM predicts an increase over the average value of over 40% at the end of discharge. Such errors may become more significant for higher current densities, dynamic load currents, and high-current pulsed operation, during which large transients and instantaneous spatial non-uniformities may be neglected by volume-averaged representations. This indicates the limitation of the Tank Model approximations and the need for their refinement for such cases. For instance, in a multi-cell stack or a large battery pack in which each individual cell is represented by the Thermal Tank Model, the objective function in a parameter estimation strategy may also incorporate error metrics between predicted and measured currents in each cell. The adjustable parameters may then be determined to minimize the errors observed in Fig. 21b, in addition to errors in $V_{cell}$.

The mismatch in current density distribution is expected to result in errors in the predictions of the State of Charge (SoC) of individual cells. This can be observed in Figs. 22c and 22d, which compares the current-distributed degree of lithiation (i.e., $\tilde{q}_i = \frac{q_i}{q_{\text{c,max}}}$). These quantities are directly proportional to the effective SoC of the cell. For the $Bi = 10$, the Tank Model deviates by approximately 10% for the “cold” cell. Errors in cell SoC will accumulate over the discharge process, given the substantial variations in instantaneous $\beta$, the integral of which determines SoC. This is despite its ability to predict the broad qualitative trends, including the change in slope of the SoC curves for both the over and under-utilized cells at $t \sim 1200$ s. A more uniform current distribution means that these deviations are not observed at the more practical $Bi = 0.01$ case, indicating the ability of the sTTM to accurately predict current and SoC distributions for cell stacks over a wide range of operating conditions. This indicates potential for use in predicting the effect of non-uniform utilization and degradation, and in integration into a BMS compared to the full sp2D model. While the sTTM is unable to predict the granular details that affect performance under aggressive conditions, these results suggest utility in predicting SoC for cell-balancing and other BMS objectives. As with the dynamic currents in individual cells, the instantaneous SoC errors may also be incorporated into the objective function in parameter estimation applications. In addition, cell-level $\tilde{q}_i$ can be directly obtained from the DAE system of the sTTM, due to the three-parameter models for solid phase transport, which directly solve for $\tilde{q}_i$ that can then be incorporated into control problem formulations.\(^{81,63}\)

In contrast, the SoC of the individual cells (or $\tilde{q}_i$) have to be computed from the sp2D model by way of volume-integrals and averaging, which will add to the computational cost. The sTTM is thus competitive with reformulated sp2D models in terms of both accuracy and computational efficiency, quantitative measures of which are presented in the next section.

At this point, it is worthwhile to reexamine the original 2 C discharge curves of Fig. 16b. It can be seen that the predictions of cell voltage exhibit close agreement, with only a slight mismatch in the final discharge time. Figure 20 suggests that the RMSE for the sTTM relative to the sp2D model is about $\sim 20$ mV. However, as this discussion shows, the agreement in voltage masks significant underlying variations in the individual cells, which are a result of the complex interplay of electrochemical and thermal phenomena. This indicates the value of a physics-based model to compute emergent cell-level properties, since the subtle electrochemical variations that give rise to complex trends in cell-level quantities can be adequately captured. These variations have clear implications for BMS and TMS, in terms of cell-balancing, monitoring individual cell SoH, preventing non-uniform degradation, and preventing overtemperature.\(^{59,40}\) The sTTM approach also provides a simpler means relative to the sp2D model to include detailed models for capacity degradation and in integration into a BMS compared to the full sp2D approach.\(^{113,50}\) The level of electrochemical detail retained by the model also makes its parameterization materially superior to equivalent circuit models\(^{10}\) for studying current imbalances in parallel configurations of cells. While the sTTM is illustrated for a case of a multi-layer pouch cell, the same formulation can also be applied to battery packs consisting of multiple cells. The model can be extended to account for interfacial and inter-cell resistances (both electrical and thermal). The modification of the Thermal Tank Model approximations to include interfacial resistances is included in the Appendix.

**Computational performance**—Representative computation times for the two models are shown in Table VIII. For a 10-cell...
The reformulated sp2D model computes a 1 C discharge curve in \( \sim 12 \) s. The sTTM is able to compute the same in \( \sim 20 \) ms, corresponding to a reduction of nearly 500x. Of note, preliminary results suggest computation times of \( \sim 700 \) ms even for a large 50-cell stack. Beyond 1 C, the accuracy of the sTTM is substantially compromised for the aggressive \( Bi = 10 \) cases as discussed previously. In addition, it is important to note that the computation time of the benchmark reformulated sp2D model is affected by the choice of the model used for solid phase transport. In this work, we used an error-free collocation approach to model the solid phase transport. Using computationally simple two and three-parameter models will cause a significant reduction in computation time for benchmark models.\(^{25,26,50,61,63}\) However, the competitiveness of the sTTM is evident, caused by the replacement of each conservation law in the sp2D model by its volume-averaged counterpart. Based on the results obtained in past work,\(^{23}\) we expect a standard Finite-Difference implementation for the p2D stack model to result in \( \sim 10000 \) DAEs, and in computation times of \( \sim 10 \) min, indicating the superiority of both the state-of-the-art sp2D models and the sTTM.

In this article, the Tank Models were obtained by the reduction of the p2D model in one spatial dimension (x). The use of a one-dimensional model instead of a 2-D model in the \( x-y \) plane is

---

Table VIII. Representative computational performance metrics for the Tank Model.

<table>
<thead>
<tr>
<th>Model and Implementation</th>
<th>Number of DAEs</th>
<th>Computation time for Bi = 10(ms)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p2D—Reformulated (10-cell stack sp2D) ( n = (2, 7, 3, 7, 2) )</td>
<td>1800–2000</td>
<td>12383 ± 312.6</td>
</tr>
<tr>
<td>Stack Thermal Tank Model (10-cell stack)(^b)</td>
<td>251(^b)</td>
<td>22 ± 0.6</td>
</tr>
</tbody>
</table>

\(^a\) Average of \( N = 3 \) simulation runs for a 1 C discharge. It must be noted that the simulation time and memory consumption is a strong function of the computing environment as well as error tolerances for both initialization and simulation. \(^b\) Including the equation for cell voltage.
justified by the aspect ratios of most practical cells. The height (vertical y dimension in Fig. 3) is usually about three orders of magnitude higher than the thickness of the assembly, which justifies the consideration of heat transfer through the thickness dimension alone. However, having discussed the importance of variations in the y–z plane for large format cells, such models must be used as electrode-scale submodel in an MSMD approach, for which the ~ms computation times of the sTTM suggests potential. It is worth noting that despite the computation time metrics achieved, the sTTM does not require additional simplifying assumptions on heat generation rates or temperature profiles. This means that the exact configuration of the cell along the thickness dimension may be directly and efficiently simulated, without assuming uniform intra-cell temperatures or electrochemically identical layers as is often done for multiple electrode pairs. Future work will evaluate the sTTM against other reduced order models of relevance for MSMD frameworks.

Conclusions and Future Work

A simplified electrochemical-thermal model for lithium-ion batteries is generated using the Tanks-in-Series methodology. The flux approximations and volume-averaged representations notwithstanding, the Thermal Tank Model is able to achieve errors below 10 mV relative to the p2D model for galvanostatic discharge rates of up to 5 C. Internal electrochemical variables and temperature predictions are accurate within 1% error. The ease of implementation of the methodology is demonstrated by extending the single cell formulation to a multi-cell stack and simulated for a large parameter space corresponding to various conditions of discharge and external heat transfer. This Stack Thermal Tank Model also results in prediction errors of <10 mV up to 4 C discharge rates and Bi ∼ 0.7. Even for aggressive conditions where Bi > 1, the predictions of temperature profiles across the stack agree within 1 K, with the chief source of errors in cell voltage being mismatches in electrolyte phase variables for T < 280 K. Predictions of emergent cell-level quantities such as current density splits and SoC are in close agreement (<1% error) for practical operating conditions, and are in qualitative agreement for more extreme cases. As with the isothermal model, the performance of the thermal models at single-cell and stack levels can be improved by parameter estimation techniques. The computational speed up over two orders of magnitude indicates the potential for real-time applications. The models can serve as replacement for SPM-like and empirical models for advanced BMS. The access to electrochemical quantities means that the models can also be used in the study of fast-charging effects on cell degradation and temperature, and incorporated into optimal-charging problems. Additionally, the models can be used to simulate performance under cycling and investigate the effects of inhomogeneities in multi-cell stacks and large battery packs. The ~ms computation time of the multi-cell models suggests promise for use in algorithms for advanced BMS functions such as SoC estimation, cell balancing, temperature control, and SoH monitoring in conjunction with physics-based degradation models.

Future work will attempt to demonstrate the single-cell and stack Thermal Tank models for these applications, especially for practically relevant cell and pack designs and parameters. A key focus is on experimental validation, followed by demonstration for parameter estimation and optimal charging. Additionally, we intend to evaluate the models against other classes of reduced-order thermal models for accuracy and efficiency metrics. A third goal is the integration of the Thermal Tank Model into MSMD frameworks, which can study more realistic temperature distribution scenarios, for the design and safety analyses of large format cells.

From a model development standpoint, interfacial thermal resistances are likely to increase the magnitude of stack temperature gradients, leading to inaccuracies in the Tank Model approximations. Additionally, while briefly touched upon, the influence of temperature and cell-level geometric, kinetic and transport parameters on the accuracy of stack-level predictions needs systematic evaluation. The derivation of the temperature approximations in the presence of interfacial resistances may be found in the Appendix, and its implementation is a key extension of current work. An additional goal is the application of the Tanks-in-Series methodology to cylindrical coordinates, characterizing accuracy and computational performance vis-à-vis both full-order and lumped models for cylindrical Li-ion cells. Combined with efficient two-dimensional schemes for the current and potential distributions, it may be possible to develop an efficient MSMD model for entire large-format cells that can be integrated into real-time frameworks. The feasibility of such an extension will also be examined in future work.

Acknowledgments

The authors would like to thank the U.S. Department of Energy (DOE) for providing partial financial support for this work through the Advanced Research Projects Agency (ARPA-E) award number DE-AR0000275, and the Advanced Battery Material Research (BMR) Program (Battery 500 Consortium). The authors would also like to thank the Clean Energy Institute (CEI) at the University of Washington and Texas Materials Institute for partial monetary support of this work. We are also grateful to Prof. Ofodike Ezekoye at UT Austin Mechanical Engineering for suggesting the need for meaningful lumped thermal models for lithium-ion batteries.

Appendix: Derivation of the Averaged Ohmic Heating Terms

In region 1, the volumetric ohmic heat generation term is given by

\[ Q_{\text{ohmic,1}} = -i_x \frac{\partial \phi_{b,1}}{\partial x} - i_y \frac{\partial \phi_{b,1}}{\partial y} \quad [A-1] \]

This expression is based on the assumption of Rao and Newman, namely that the ohmic heat dissipation is due to potential gradients in both solid and liquid phases, and concentration effects are ignored.

Following the general Tanks-in-Series averaging procedure in one-dimension, we have

\[ Q_{\text{ohmic,1}} = \frac{1}{l_1} \int_{x=0}^{x=l} Q_{\text{ohmic,1}} \, dx = \frac{1}{l_1} \left( \int_{x=0}^{x=l} i_x \frac{\partial \phi_{b,1}}{\partial x} \, dx - \int_{x=0}^{x=l} i_y \frac{\partial \phi_{b,1}}{\partial y} \, dx \right) \quad [A-2] \]

As mentioned in our previous article, the solid phase ohmic drop is generally negligible compared to that of the liquid phase. Therefore, the solid phase ohmic contribution may also be neglected, and Eq. A-2 becomes

\[ Q_{\text{ohmic,1}} \approx - \frac{1}{l_1} \int_{x=0}^{x=l} i_y \frac{\partial \phi_{b,1}}{\partial y} \, dx \quad [A-3] \]

Integrating by parts, we have

\[ Q_{\text{ohmic,1}} = -\left( \frac{1}{l_1} \right) i_{y,12} \phi_{b,1,1,x=l} - i_{y,0} \phi_{b,1,1,x=0} \]

+ \left( \frac{1}{l_1} \right) \int_{x=0}^{x=l} \frac{\partial i_{y,1}}{\partial x} \, dx \phi_{b,1} \, dx \quad [A-4] \]

From Fig. 2, we have, \( i_{y,12} = i_{\text{app}} \) and \( i_{y,12} = 0 \). Using these relations, and the standard notation, we obtain
\[ Q_{\text{ohmic,1}} = -\left( \frac{1}{l_1} \right) (i_{\text{app}} \phi_{1,12}) + \left( \frac{1}{l_1} \right) \int_{x=0}^{x=l_1} \frac{\partial i_{1,12}}{\partial x} \phi_{1,12} \, dx \quad [A\text{-}5] \]

Now, we can simplify the integral in the above equation by using Eq. 49 in Ref. 43

\[ Q_{\text{ohmic,1}} = -\left( \frac{1}{l_1} \right) (i_{\text{app}} \phi_{1,12}) + (F \alpha_{1j} \phi_{1,12}) \quad [A\text{-}6] \]

Furthermore, using the volume-averaged relation, we have

\[ Q_{\text{ohmic,1}} = -\left( \frac{1}{l_1} \right) (i_{\text{app}} \phi_{1,12}) + (F \alpha_{1j} \phi_{1,12}) \quad [A\text{-}7] \]

Using the standard Tank Model assumption \( \phi_{1,12} \approx \frac{\phi_{1,12}}{F \alpha_{1j}} \), and the relation for volume-averaged pore-wall flux \( \phi_{1,12} \approx \frac{\phi_{1,12}}{F \alpha_{1j}} \), the equation reduces to

\[ Q_{\text{ohmic,1}} = \left( i_{\text{app}} - \phi_{1,12} \right) \quad [A\text{-}8] \]

Analogous expression may be derived for the separator and negative electrodes as

\[ Q_{\text{ohmic,3}} = \left( i_{\text{app}} - \phi_{1,23} \right) \quad [A\text{-}9] \]

\[ Q_{\text{ohmic,2}} = \left( i_{\text{app}} - \phi_{1,12} \right) \quad [A\text{-}10] \]

The ohmic heating term for the separator is slightly modified due to the lack of a reaction term, i.e. \( \phi_{1,23} \approx 0 \). Thus, a constant current density \( i_{\text{app}} \) is carried entirely by the liquid phase.

Appendix: Accounting for Interfacial Thermal Resistances

In the presence of thermal resistances at the interfaces, there is an interface temperature discontinuity which must be accounted for, and which changes the Bi further. This example is illustrated for the positive electrode, and may be identically applied to the other domains.

The thermal resistance boundary conditions are given by

\[ q_{1,x=l_1} = q_{2,x=l_2} = \frac{(T_{1,x=l_1} - T_{2,x=l_2})}{R_{1,12}} \quad [A\text{-}11] \]

Given the requirement for flux continuity. Using the Tank Model flux approximations gives us two relations for determination of Temperature on either side of the interface

\[ T_{1,x=l_1} - T_{2,x=l_1} = \left( \frac{1}{R_{1,12}} \right) \left( -\lambda_1 (T_{1,x=l_1} - T_{1}) \right) \quad [A\text{-}12] \]

Solving these two equations yields the interfacial values as

\[ T_{1,x=l_1} = \frac{2R_{1,12} \lambda + l_2 T_{1} + l_1 T_{2}}{2R_{1,12} \lambda + l_2 + l_1} \]

\[ T_{2,x=l_1} = \frac{2R_{1,12} \lambda + l_2 T_{1} + l_1 T_{2}}{2R_{1,12} \lambda + l_2 + l_1} \quad [A\text{-}13] \]

Where the standard film thickness approximation, \( \delta_{1,2} = \frac{l_1}{2} \) has been applied. In the absence of interfacial resistance, \( R_{1,12} = 0 \), and we recover the original condition \( T_{2,x=l_1} = T_{2,x=l_2} = T_{2} \).

Equation [A-13] and analogous expressions for the other domains can now be substituted into the volume-averaged heat balances of Eqs. 16–18 to yield the augmented energy balances.

**ORCID**

Akshay Subramaniam https://orcid.org/0000-0002-9306-7436
Venkata R. Subramaniam https://orcid.org/0000-0002-2092-9744

**References**


