Modelling the Diffusion Overpotential in Li-ion Batteries using a State-Space System with Receding Horizon

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Abstract

Equivalent-circuit model representations of the diffusion overpotential in lithium-ion batteries often use fractional-order system dynamics, which can have high computational cost. Thus a novel equivalent circuit is proposed, named the ‘receding-horizon diffusion’ (RHD) model. The model is defined with a series resistor, a resistor-capacitor pair, and a diffusion element. For the first time, a state-space discrete-time recursive formulation of diffusion is obtained. A four-fold verification of the prediction accuracy and physical relevance is performed using simulated and experimental data with a range of C-rates, temperatures, and degradation levels. It is shown that the RHD model can be used to track voltage and analyze the solution, charge-transfer, and diffusion overpotentials in real time, outperforming standard RC-pair models in both accuracy and interpretability with little increase in computation cost. The RHD model could be easily integrated into battery management systems in electric vehicles and used in standard state estimation techniques.

Keywords: Lithium batteries, Battery management systems, Equivalent circuits, State-space methods, Electrochemical processes

1. Introduction

Lithium-ion battery (LIB) models form the basis of most battery management systems (BMS) [1]. The BMS depends on accurate models to perform state estimation [2]. Battery models can also be used to provide insight into cell degradation [3], which could allow for advanced degradation-reduction techniques [4]. There are 2 popular model types: physics-based models (PBM) and equivalent circuit models (ECM). PBMs are highly accurate and offer insight into internal cell processes, but face challenges in real-time use [5, 6]. ECMs are especially popular in electric vehicle (EV) applications for their simplicity and speed [7]. More recently, fractional-order models (FOM) and physically-meaningful ECMs have been proposed that can quantify electrochemical overpotentials in the cell [8]. These models offer greater interpretability than standard ECMs without significantly increasing computation time.

The ‘NRC model’ is a basic ECM consisting of one series resistor and N pairs of resistors and capacitors in parallel (known as RC pairs), where typically N > 2. Estimation and simulation of the model parameters is performed on time-domain voltage data using techniques such as recursive least-squares [9]. Computation of the NRC model is fast due to its linear discrete state-space formulation. The NRC model can predict battery voltage with high accuracy, but lacks interpretability — meaning it yields limited information on degradation-related internal processes, especially diffusion. This suffices for a conventional BMS, but tracking and predicting battery degradation is increasingly important for advanced BMS diagnostics [4].

FOMs are a more advanced model used for frequency-domain data obtained through electrochemical impedance spectroscopy (EIS). EIS is a time-consuming process mainly used for laboratory studies [10]. The frequency-varying impedance is modelled with a FOM such as the Randles circuit, whose parameters can be used to provide insight into degradation modes in the cell [11]. FOMs in-
clude a constant-phase element (CPE), shown in Fig. 1a. The CPE is defined by a fractional-order transfer function, which is shown to accurately capture the charge transfer and diffusion overpotentials [12]. In Randles circuits, a 0.5-order CPE named the Warburg impedance is added. FOMs face challenges in BMS implementation because frequency-domain data is difficult to obtain in real-time. Since FOMs can provide insight into overpotentials and degradation, time-domain identification of FOMs was studied in [13]. This could allow for real-time insight into degradation modes.

Following the work in [13], other time-domain identification methods have been considered for physically-meaningful FOMs. In [14], parameters are obtained using several pulse-perturbations at multiple polarization points, lasting 16s total. While faster than EIS measurements, pulses may be difficult to implement in an EV BMS. In [15], least-squares and gradient methods for parameter identification of an FOM are proposed, but have high computational cost. Fast FOM parameter identification evidently requires new approaches which may be computationally expensive.

As an alternative to FOMs, reduced-order physics-based descriptions of the diffusion overpotential are combined with NRC elements. By capturing overpotential dynamics, modelling accuracy is increased without much increase in computational cost [16]. Various formulations of diffusion are presented in [8, 17, 18, 19]. The models in [17] and [19] use at least 4 parameters to characterize diffusion, but [8] develops the ‘DNRC model’, which captures diffusion using only 1 parameter. While promising, the models face challenges in computation time and interpretability. There remains a need for physically-meaningful ECMs that can describe the diffusion overpotential without sacrificing the simplicity of NRC models.

1.1. Contributions and outline

This article proposes two novel definitions of the diffusion overpotential derived from results first obtained in [8]. This leads to two ECMs named the ‘convolution-defined diffusion’ (CDD) and ‘receding-horizon diffusion’ (RHD) model, both shown in Fig. 1b. The CDD model accurately describes the diffusion overpotential using convolution, while the RHD model presents a linear receding-horizon discrete state-space formulation that approximates convolution. For the first time, to the best of our knowledge, a linear description of diffusion is achieved with only 1 modelling parameter. The RHD model is accurate, fast, and physically meaningful. A standard BMS could easily implement the RHD model to track electrochemical overpotentials in real-time.

The article continues in Section 2 with derivation of the CDD model from first principles. In Section 3, the RHD model is derived. In Section 4, verification results are presented and discussed. The article is concluded in Section 5.

2. Convolution-Defined Diffusion Model

The CDD model extends electrochemical principles first described in [8, 20]. Lithium-ion diffusion is quantified with the diffusion constant $A_D$, given
Figure 1: Battery equivalent circuits, showing (a) Fractional-order model (FOM) with a constant-phase element (CPE) and Warburg impedance, and (b) Proposed receding-horizon diffusion (RHD) model with labelled overpotentials

Table 1: Key electrochemical parameters with typical values for a nickel-manganese cobalt (NMC) cell

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>Lithium-ion diffusion coefficient</td>
<td>—</td>
<td>m²s⁻¹</td>
</tr>
<tr>
<td>1/β</td>
<td>Max stoichiometric added lithium</td>
<td>[0, 1]</td>
<td>—</td>
</tr>
<tr>
<td>v_M</td>
<td>Molar volume of NMC</td>
<td></td>
<td>cm³</td>
</tr>
<tr>
<td>M_NMC</td>
<td>Molar mass of NMC</td>
<td>96.46</td>
<td>g mol⁻¹</td>
</tr>
<tr>
<td>ρ_NMC</td>
<td>Density of NMC</td>
<td>4.7</td>
<td>g cm⁻³</td>
</tr>
<tr>
<td>S</td>
<td>Active surface area</td>
<td></td>
<td>cm²</td>
</tr>
<tr>
<td>ε_AM</td>
<td>Volume fraction of active material</td>
<td>[0, 1]</td>
<td>—</td>
</tr>
<tr>
<td>L_agg</td>
<td>Agglomerate size</td>
<td></td>
<td>μm</td>
</tr>
<tr>
<td>ε_e</td>
<td>Electrode volume</td>
<td>—</td>
<td>cm³</td>
</tr>
<tr>
<td>F</td>
<td>Faraday’s constant</td>
<td>96 485</td>
<td>C mol⁻¹</td>
</tr>
</tbody>
</table>

by

$$A_D = \frac{2βv_M}{SF\sqrt{Dπ}}$$ (1)

where the parameters are defined in Table 1. It was shown using the DNRC model in [8] that each current step change at time $t_n \leq t$ incites a diffusion state $ψ_n(t)$ defined as

$$ψ_n(t) = ζ_n \sqrt{t - t_n}$$ (2)

with the diffusion state amplitude $ζ_n$ at step index $n$. Importantly, [8] also shows that amplitude $ζ_n$ depends on the value of the step change $ΔI$ and the gradient of the open-circuit voltage (OCV) curve, given by

$$ζ_n = ΔI(t_n)∇V_{OC}(t_n)$$ (3)

where we define

$$ΔI(t_n) = i(t_n) - i(t_n - Δt)$$

$$∇V_{OC}(t_n) = \frac{∂V_{OC}}{∂SoC}(SoC(t_n))$$ (4)

where $V_{OC}$ is the OCV, SoC is the state of charge, $Δt$ is the sampling interval, and $i$ is the cell current.

The DNRC diffusion overpotential is then given by

$$V_{DNRC}(t) = A_D \sum_{n=1}^{N_{step}} ψ_n(t)$$ (5)

where $N_{step}$ is the total number of step changes. It is undesirable to use a sum of accumulated states. Since the DNRC model requires each current step change to be identified and labelled, for an arbitrarily-varying cell current this formulation can be computationally prohibitive, hence the need for CDD.

To arrive at the CDD model, the input current is treated as a continuous-time system sampled with zero-order hold (ZOH). The ZOH-modified cell current is given by the sum of rectangle pulses, denoted as the function rect(·),

$$i(t) = \sum_{k=0}^{∞} i(t_k) \cdot \text{rect}\left(\frac{t - t_k - Δt}{Δt}\right)$$ (6)

for $t > 0$. At each sampling index $k$, there are now two step changes in current corresponding to the rising and falling edge of the ZOH pulse. Thus the
diffusion overpotential becomes

\[ V_D(t) = A_D \sum_{k=0}^{\infty} \left( \psi_k(t) + \psi'_k(t) \right) \]  
(7)

where \( \psi_k \) and \( \psi'_k \) are the rising and falling edge diffusion states due to the ZOH pulse at index \( k \). Similarly, the diffusion state amplitude at the rising edge is given by

\[ \zeta_k = i(t_k) \nabla V_{OC}(t_k) = \zeta(t_k) \]  
(8)

which is equal and opposite at the falling edge, \( \zeta_k' = -\zeta_k \). Note that \( \zeta \) can now be described as a function of time. Substituting (8) into (2) yields the sum of the rising and falling edge states,

\[ \psi_k(t) + \psi'_k(t) = \zeta(t_k) g_z(t - t_k) \]  
(9)

for \( t > t_k \), where we define the unit impulse response

\[ g_z(t) = \sqrt{1 - \frac{t}{\Delta t}} \]  
(10)

The aggregated diffusion overpotential is therefore the infinite sum of the ZOH-modified responses, which represents convolution, denoted by \( \ast \). Substituting (9) into (7) yields the CDD overpotential,

\[ V_D(t) = A_D \sum_{k=0}^{\infty} \zeta(t_k) g_z(t - t_k) = A_D \cdot \zeta(t) * g_z(t) \]  
(11)

Equation (11) shows that the diffusion overpotential can be represented as the convolution of the diffusion state amplitude \( \zeta \) with the unit impulse response \( g_z \). Compared to the DNRC formulation, convolution is computed much faster given an arbitrary current input. Convolution is not suitable for real-time, however, because the entire current history must be stored. A recursive definition is thus preferred.

The CDD model is linked to FOMs due to its fractional-order impulse response. The Laplace transform \( G(s) \) of the continuous-time impulse response is given by

\[ G(s) = \mathcal{L} \left( \lim_{\Delta t \to 0} \frac{g_z(t)}{\Delta t} \right) = \mathcal{L} \left( \frac{1}{2\sqrt{t}} \right) = \sqrt{\frac{\pi}{4}} s^{-1/2} \]  
(12)

which represents a semi-integral in the time-domain, expressible using fractional calculus. This agrees with the results in [21].

3. Receding-Horizon Diffusion Model

The RHD model state equations are given by

\[ x(t_{k+1}) = Ax(t_k) + Bu(t_k) \]
\[ y(t_k) = Cx(t_k) + Du(t_k) \]  
(13)

\[ x(t_k) = \begin{pmatrix} x_\ell(t_k) \\ x_\varnothing(t_k) \end{pmatrix}, \quad u(t_k) = \begin{pmatrix} i(t_k) \\ i(t_{k-1}) \end{pmatrix} \]  
(14)

\[ A = \begin{pmatrix} A_\ell & 0 \\ 0 & A_\varnothing \end{pmatrix}, \quad B = \begin{pmatrix} B_\ell \\ B_\varnothing \end{pmatrix}, \quad C = \begin{pmatrix} C_\ell & C_\varnothing \end{pmatrix} \]  
(15)

where the output is the sum of all overpotentials,

\[ y(t_k) = V_o(t_k) + V_{ct}(t_k) + V_D(t_k) \]  
(16)

The cell terminal voltage \( V_o \) is then given by

\[ V_o(t_k) = V_{OC}(t_k) - y(t_k) \]  
(17)

When \( N = 2 \) RC-pairs are used, the variables \( A_\ell, B_\ell, C_\ell, \) and \( D_\ell \) are given by standard NRC equations,

\[ A_\ell = \begin{pmatrix} e^{-\frac{\Delta t}{\tau_\ell}} & e^{-\frac{\Delta t}{\tau_{\ell/2}}} \\ e^{-\frac{\Delta t}{\tau_{\ell/2}}} & e^{-\frac{\Delta t}{\tau_\ell}} \end{pmatrix}, \quad B_\ell = \begin{pmatrix} 1 - e^{-\frac{\Delta t}{\tau_\ell}} & 0 \\ 0 & 1 - e^{-\frac{\Delta t}{\tau_{\ell/2}}} \end{pmatrix} \]  
(18)

\[ C_\ell = \begin{pmatrix} R_1 & R_2 \end{pmatrix}, \quad D_\ell = \begin{pmatrix} R_0 & 0 \end{pmatrix} \]  
(19)

Note that \( x_\ell \in \mathbb{R}^N \) is the solution and charge transfer state vector, \( A_\ell \in \mathbb{R}^{N \times N} \) is a diagonal matrix, \( B_\ell \in \mathbb{R}^N \) is a column vector, and \( C_\ell \in \mathbb{R}^N \) and \( D_\ell \in \mathbb{R}^2 \) are row vectors.

The variables \( x_\ell, A_\ell, B_\ell, \) and \( C_\ell \) describe the diffusion element in the RHD model and are formulated below. As noted earlier, the DNRC model is infeasible for long time scales due to the constantly-growing state vector. Meanwhile, the CDD model requires the entire current history to be stored. These disadvantages are avoided by applying a receding-horizon. All states beyond the horizon are assumed to saturate at some constant value. Only states within the horizon are tracked, and an offset term is used to store the saturated states.

The recursive-discrete form of a diffusion state is obtained from ZOH discretization of (2). Due to the non-linearity of square-root dynamics, it can
be shown that the discrete-recursive definition is a piece-wise function,

\[
\psi_n(t_{k+1}) = \begin{cases} 
\psi_n(t_k)\sqrt{1 + \frac{1}{k-n}} & k > n \\
\zeta_0\sqrt{\Delta t} & k = n \\
0 & k < n 
\end{cases} \quad (20)
\]

For a continuously-varying current input, there is a current step at each \(k\), so there is no longer a need to track the \(n^{th}\) current step. Thus from (3) and (14) we can define

\[
\psi_k(t_{k+1}) = b_v(t_k)u(t_k) \quad (21)
\]

where \(b_v(t_k) \in \mathbb{R}^2\) is a row vector dependent on the time step that introduces the OCV gradient and differential current into the RHD model,

\[
b_v(t_k) = \nabla V_{OC}(t_k)\sqrt{\Delta t} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \quad (22)
\]

For a horizon with a length of \(M\) time steps, the diffusion overpotential becomes

\[
x_{\nu}(t_{k+1}) = A_\nu x_{\nu}(t_k) + B_\nu u(t_k) \\
V_D(t_k) = C_\nu x_{\nu}(t_k) \quad (23)
\]

\[
x_{\nu}(t_k) = \begin{pmatrix} D_\nu(t_k) \\ x_{\nu,M}(t_k) \\ \vdots \\ x_{\nu,1}(t_k) \\ x_{\nu,0}(t_k) \end{pmatrix} \quad (24)
\]

\[
A_\nu = \begin{pmatrix} 1 & a_M & 0 & 0 & 0 & \cdots & 0 \\ 0 & 0 & a_M & 0 & 0 & \cdots & 0 \\ 0 & 0 & 0 & a_{M-1} & 0 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & 0 & 0 & \cdots & a_2 \\ 0 & 0 & 0 & 0 & 0 & \cdots & 0 \\ 0 & 0 & 0 & 0 & 0 & \cdots & 0 \end{pmatrix}
\]

\[
B_\nu = \begin{pmatrix} 0 \\ \vdots \\ 0 \\ b_v(t_k) \end{pmatrix}, \quad C_\nu = A_D \begin{pmatrix} 1 & \cdots & 1 \end{pmatrix} \quad (25)
\]

where \(x_{\nu} \in \mathbb{R}^{M+2}\) is a column vector, \(A_\nu(k) \in \mathbb{R}^{(M+2) \times (M+2)}\) is a square matrix, \(B_\nu(k) \in \mathbb{R}^{(M+2) \times 2}\) is a tall matrix with \(M+2\) rows and 2 columns, \(C_\nu \in \mathbb{R}^{M+2}\) is a row vector, \(D_\nu\) is a scalar, and \(a_m\) is a scalar, derived from (20), that is defined by the relative sampling time \(m\),

\[
a_m = \sqrt{1 + \frac{1}{m}} \quad (26)
\]

The parameter \(A_D\) in \(C_\nu\) is the only modelling parameter that must be identified. The step horizon \(M\) is treated as a tuning parameter that is fixed before implementation of the RHD model. Step horizon corresponds to a length of time, so for a 10s horizon and a sampling interval of 0.1 s, \(M = 100\).

Dynamic processes occur in the state vector that are inherent in the matrix \(A_\nu\). As \(k\) increases, \(A_\nu\) advances the states by ‘shifting’ the state vector. At each time step, one state saturates and another is initialized. Saturated states are stored in the offset term \(D_\nu\). This offset term is an accumulated sum of the saturated values. In contrast to the CDD model, the RHD model only requires a fixed number of states that are updated recursively in discrete-time. Thus a completely linear state-space definition is achieved.

4. Verification Results and Discussion

Four-fold verification is performed using six distinct results. First, the CDD model is linked to diffusion by recovering the diffusivity in a PBM and through qualitative Nyquist plots. Second, the CDD model yields strong parameter variation trends. Third, the RHD model exactly approximates CDD for a sufficient horizon length. Finally, the RHD model increases prediction accuracy compared to NRC models and can track individual overpotentials. A mix of simulated and experimental data is used to achieve the results.

4.1. Linking CDD model to diffusion

The first link between CDD and diffusion is demonstrated with PBM-simulated data. Unlike in real systems, the aggregated diffusivity of the cell is known in a PBM. Thus the apparent diffusivity \(\hat{D}\) as calculated from the diffusion constant \(A_D\) is compared with the true aggregated diffusivity. Results are shown in Fig. 2 with simulated voltage shown in 2a. The mean absolute percent error (MAPE) of the predicted voltage is bounded by 1% for all pulses. The highest error results from low diffusivities and high SoC which may cause OCV non-linearities not captured by the CDD model. Besides these extremes, the CDD model accurately
Figure 2: Comparison between the CDD-0RC model and PBM model, showing (a) PBM-simulated voltage response and predicted CDD-0RC voltage and (b) Apparent diffusivity predicted by CDD-0RC model compared with the true PBM diffusivity.

Figure 3: Nyquist curves from frequency analysis of simulated CDD-1RC time-domain data, showing overpotential variations in (a) Solution, (b) Charge transfer, and (c) Diffusion

Figure 4: Analysis of aged NMC cells at various SoC using the CDD-1RC model, showing (a) observed cell voltage and predicted CDD-1RC voltage, (b) Absolute percent error of the predicted voltage color-coded by SoH, and (c)-(d) CDD-1RC modelling parameters plotted against SoH and SoC
models the PBM voltage response. The apparent diffusivity trendline demonstrates strong agreement with the true diffusivity. Variation in the individual estimates of apparent diffusivity is due to SoC-varying initial states such as the initial concentration of lithium-ions. Despite SoC variation, the CDD model diffusion constant $A_D$ is shown to be directly linked to the internal diffusivity, verifying the CDD model hypothesis.

The second result is from frequency analysis of CDD-simulated data. In electrochemical impedance spectroscopy, the overpotentials are clearly observed in the frequency domain Nyquist curves [10]. Only diffusion is known to affect the low-frequency 'tail'. Therefore the frequency spectrum of the simulated CDD model should yield distinct behavior in the Nyquist curves. Results are shown in Fig. 3. It can be seen that the parameters affect the Nyquist plot as expected. Ohmic resistance $R_0$ shifts the x-axis crossing, $R_1$ affects the size of the mid-frequency semi-circle, and $A_D$ affects the low-frequency tail, again suggesting that $A_D$ is uniquely linked to diffusion.

4.2. Using CDD to track aging parameters

Aging data is used to demonstrate how the CDD and RHD models can track cell parameters over the cell’s lifetime. This is important for cell diagnostics. Different usage profiles may result in different parameter trends, which can inform optimal cell cycling conditions. Results for cells degraded at low temperature and SoC are shown in Fig. 4. The MAPE of the predicted voltage is below by 0.5% for all pulses. Percent error spikes at transitions, but otherwise remains low. There are very strong trends in the CDD-1RC parameters. Resistances increase as state of health (SoH) decreases, while capacitance decreases. The diffusion constant $A_D$, which varies inversely with diffusivity, is seen to increase as SoH decreases. This agrees with the observations in [22], where lithium-ion diffusion may be slowed by degradation processes.

4.3. Showing RHD can exactly approximate CDD

Simulations of the RHD and CDD model are compared to demonstrate how the receding horizon approximates convolution. Two waveforms are used for comparison: sawtooth and current steps. Results are shown in Fig. 5. Approximation error decreases to zero as the horizon length approaches the data length of 300 s. The sawtooth wave is approximated more accurately than current steps. This suggests that the RHD model is slightly more suited to inputs with constant non-zero gradients, which is often the case in real systems. Approximation error is small regardless of the input. Rather than require the entire current input to be known a posteriori, the RHD model only requires two samples of the input and a fixed number of states for a highly accurate discrete-recursive approximation of convolution.

4.4. Demonstrating RHD accuracy and overpotential tracking

Drive cycle data is first used to compare real-time RHD model performance to that of conventional NRC models. The C-rates for four distinct 2-minute drive cycles – US06, urban dynamometer driving schedule (UDDS), LA92, and highway fuel economy test (HWFT) – applied at $\{0, 10, 25\}^\circ C$ are shown in Fig. 6a. Computation time and MAPE of the RHD model are assessed using the various datasets. Results for computation time and error using the drivecycles are shown in Fig. 6b. RHD models have higher computation time due to the larger state vector, but computation time is traded-off for accuracy. The MAPE of the RHD models is consistently lower than or bounded by corresponding NRC error, showing that the proposed diffusion element increases modelling accuracy. The exact improvement is most easily observed for the 1 RC-pair models, and is data-dependent. For the lower current cycles, UDDS and LA92, error decreases with the horizon length. In contrast, the optimal horizon length for US06 and HWFT cycles is around 40 s. This could reflect real-life LIB diffusion processes, which have time-constants of similar orders [17].

The second use of drive cycle data is for tracking overpotentials. Results of overpotential analysis using the LA92 drivecycle are shown in Fig. 7 for the RHD-1RC with a 40 s horizon. Maximum error is less than 0.51%. Overpotentials are easily disaggregated from the predicted voltage, showing that different processes dominate at different times. This agrees with results in [23] and can be used to gain insight into internal cell processes.

5. Conclusion

A novel ECM named the CDD model was shown to capture the diffusion overpotential in LIB cells
Figure 5: Results showing how RHD approximates CDD, with (a) Simulated current waveforms and variation of voltage MAPE between RHD and CDD, and (b) Voltage and percent error using various RHD horizon lengths (in color) compared with the CDD output (in black).

Figure 6: Comparison between proposed RHD model and NRC models, showing (a) Drive cycle data, (b) Computation time, and (c) MAPE for various horizon lengths, where length 0 refers to the NRC model, and non-zero length refers to the RHD model.

Figure 7: Overpotential analysis for LA92 data using RHD-IRC model with a 20 s horizon, showing (a) Voltage prediction and percent error and (b) Variation of overpotentials over time.
using convolution. For real-time implementation, the RHD model was formulated with a linear discrete-time recursive state-space system. This is the first linear representation of diffusion to use a single modelling parameter without fractional-order computations. Verification using simulated and experimental data shows that the RHD model is fast, accurate, and general-purpose. It can be easily adapted to existing BMS state estimation techniques such as Kalman filters to offer further insight into battery degradation.

Future work includes real-world verification in a wider operating range and optimization of the state-space system. More extreme temperatures and current rates can be applied. Subsampling techniques could be used to reduce the size of the diffusion state vector. Finally, the RHD model can be integrated with advanced diagnostics in a real EV or grid system. This could give a greater understanding of internal cell dynamics with small increases in computation time.

**Methods**

**Parameter fitting**

Parameter estimation of all models is performed using the scatter-search non-linear global optimization algorithm [8, 24]. This is represented as

\[
\begin{align*}
\text{minimize} & \quad f(\theta) \\
\text{subject to} & \quad \theta \succ 0 
\end{align*}
\]  

(27)

We define

\[
\begin{align*}
\theta &= \| r - y \|_2^2 + w \| r' \|_2^2 \\
r &= y - \hat{y}(\theta)
\end{align*}
\]  

(28)

where \( f \) is the objective function, \( y \) and \( \hat{y} \) are the observed and predicted data vectors, \( \theta \) is the parameter vector, \( \| r \|_2^2 \) is the sum of squared residuals, \( \| r' \|_2^2 \) is the sum of squared residual differences, and we set the weighting \( w = 1 \).

**Physics-based model**

A coupled agglomerate-scale and electrode-scale continuum PBM for an NMC cell, described in [25, 26], is used. Diffusivities used to simulate the voltage are in the range \( \{0.2, 0.3, \ldots, 1\} \times 10^{-10} \), while the nominal SoC ranges from 0.1 to 0.9. For simplicity, the PBM does not capture charge transfer dynamics so no RC pairs are used in the CDD model, hence the name ‘CDD-0RC’. The only modelling parameters are \( R_0 \) and \( A_D \). Apparent diffusivity \( \hat{D} \) is calculated from the CDD parameter \( A_D \),

\[
\hat{D} = \frac{4}{\pi} \left( \frac{\beta_{eM}}{SFAD} \right)^2
\]  

(29)

where the parameters are defined in Table 1 and \( 1/\beta = 0.55 \), \( \varepsilon_{AM} = 0.306 \), and \( L_{agg} = 1 \mu m \). Unlike the DNRC model in [8], no underestimation prefactor is required. This is because saturation of the diffusion overpotential in the CDD model, unlike in the DNRC model, is guaranteed by the finite unit impulse response.

**Frequency-domain analysis**

The complex frequency-varying impedance \( Z(s) \) is given by

\[
Z(s) = \frac{V(s)}{I(s)}
\]  

(30)

where \( s \) is the complex angular frequency, and \( V(s) \) and \( I(s) \) are the complex frequency spectra of the voltage and current. To obtain \( V(s) \) and \( I(s) \), there are three steps:

1. Simulate time domain pulse voltage responses with CDD-1RC model lasting several minutes and with sampling frequency 10 Hz. Pulses are used because they excite a wide range of frequencies.
2. Apply Hamming window to reduce spectral noise
3. Discrete fast Fourier transform of the Hamming-windowed voltage and current data

The Nyquist curve is a plot of the negative imaginary impedance \( -\text{Im}(Z) \) against real impedance \( \text{Re}(Z) \). A range of parameters are used, with \( R_0 = \{0.02, 0.04, 0.08\} \Omega \), \( R_1 = \{0.01, 0.02, 0.03\} \Omega \), \( C_1 = 1000 \mu F \), and \( A_D = \{9, 15, 25\} \times 10^{-4} \text{A}^{-1} \text{s}^{-0.5} \). To observe the effects of \( R_0 \), \( R_1 \), and \( A_D \), one parameter is varied while the others are held constant. This allows the frequency behavior to be clearly observed.

**Tracking cell degradation**

Cell aging data is collected from 3 commercial 2.7 Ah lithium-nickel-manganese-cobalt (NMC) oxide cells (Panasonic NCR18650PF) held at 10°C. Cells are degraded by low-voltage cycling at 1 C-rate, which can represent incomplete charging and high depth-of-discharge. This usage profile could be common in portable electronics. There are 14
unique SoH in the range [0.78, 1]. At each SoH, unipolar charge pulses are applied to the cell at 9 SoC in the range [0.1, 0.9]. The CDD-1RC model parameters are then estimated from the voltage responses. Parameter estimation is performed using the scatter-search non-linear global optimization algorithm [8, 24].

Approximating concelation

Data is simulated from a virtual CDD-2RC cell’s voltage response to a current stimulus. Identical parameters are used in both models but the RHD horizon length is varied from 10s to 300s, with values $R_0 = 0.02 \Omega$, $R_1 = 0.1 \Omega$, $R_2 = 0.01 \Omega$, $C_1 = 7 \times 10^3 F$, $C_2 = 1 \times 10^3 F$, and $A_D = 0.001 \Lambda^{-1} e^{-0.5}$. The horizon-length-varying error between the RHD approximation and CDD simulation is then examined for both sawtooth and step waveforms.

Drive cycle analysis

Drive cycle data is obtained from [27], where a fresh 2.9 Ah NMC cell (Panasonic 18650PF) is tested in a thermal chamber. The four drive cycles are chosen to assess the model at multiple temperatures and C-rates. The US06 cycle represents high-acceleration driving; UDDS represents urban driving; LA92 is similar to UDDS but more California-centric; and the HWFT represents highway driving. The two-minute portions were applied to the fully rested cell.

References


[26] Z. Hui, K. S. Mayilvahanan, Y. Yang, A. C. West, Determining the length scale of transport impedances in li-ion electrodes: Li(Ni0.33Mn0.33Co0.33)O2, J. Electrochem. Soc. 167 (2020).