A Reduced Order Electrolyte Enhanced Single Particle Lithium Ion Cell Model for Hybrid Vehicle Applications

Tanvir R. Tanim¹, Christopher D. Rahn² and Chao-Yang Wang³

Abstract—Low order, explicit models of lithium ion cells are critical for real-time battery management system (BMS) applications. This paper presents a linearized ⁷th order, electrolyte enhanced single particle model (ESPM) in an explicit impedance transfer function format with electrolyte diffusion effect. The impedance transfer function coefficients are explicit in terms of the model parameters, simplifying the implementation of temperature dependence in the ESPM (ESPM-T). The models are compared with a commercially available finite volume based model and results show accurate matching of pulse responses over a wide range of temperature and C-rates.

I. INTRODUCTION

Li-ion batteries are the leading candidates for HEVs and PHEVs, as they offer 40 - 50% weight reduction and 30 - 40% volume reduction along with superior coulometric and energy efficiency compared to their closest rivals, Ni-MH batteries [1]. Hybrids require advanced, real-time battery management systems (BMS) that ensure safe and efficient power utilization, estimate state of charge (SOC) and state of health (SOH), and balance cell strings [1]. Accurate cell models that capture the fast cell dynamics in HEVs are critical for high performance BMS design. BMS are often based on equivalent circuit models [2], [3], [4], [5] that lack the important underlying physiochemical processes of the cell and require extensive empirical parametrization for precise estimation.

A fundamental electrochemical cell model [6], [7] could be an accurate and reliable candidate for model based BMS design. Computational time and expense of solving the underlying highly nonlinear and coupled partial differential equations (PDEs), however, limit their use in real time BMS applications. Reduced order models have been developed by many researchers that predict the cell response with varying degrees of fidelity and model complexity. Smith et al. [8] obtains a control-oriented, isothermal, reduced ⁸th order model in state variable form using residue grouping. Klein et al. [9] reduce the full electrochemical model by assuming constant electrolyte concentration and approximating solid phase diffusion using volume averaging. Incorporating a temperature corrective term in the energy equation enables good agreement with a hybrid cycle at moderate C-rates [10].

The single particle model (SPM) studied by many researchers [11], [12], [13], [14] is a simplified, physics-based, fundamental model. The two cell electrodes are modeled by two spherical particles and associated diffusion equations are solved assuming average electrochemical reaction rate. The electrolyte dynamics are completely ignored by assuming instantaneous Li-ion transfer from one electrode to the other, leading to significant error at higher C-rates [11]. Rahimian et al. [15] propose an improved isothermal SPM by adding polynomially approximated electrolyte dynamics. Their improved SPM reduces to 13 differential algebraic equations (DAEs) and are solved in COMSOL Inc. Marcicki et al. [16] recently added ⁹th order truncated electrolyte dynamics to a SPM from a cell specific transcendental transfer function.

Most of the previously developed SPMs do not consider the electrolyte dynamics and are isothermal. Few researchers such as [15], [16] attempted to incorporate the electrolyte dynamics into the SPM model. On the other hand, isothermal models can be highly inaccurate at low temperatures. A BMS capable of achieving excellent SPM model based SOC estimation at room temperature, for example, would produce erroneous results during cold starts. This paper (i) incorporates electrolyte dynamics into a conventional, isothermal SPM of a Li-ion cell; (ii) simulates the performance compared to a commercial code (EC Power, AutoLion-ST⁷⁰⁰); (iii) adds temperature dependent parameters to the model; and (iv) demonstrates the improved performance of this enhanced SPM with temperature effect (ESPM-T). Integral method analysis (IMA) is used to solve the Li-ion diffusion equation in the electrolyte domain. Temperature is an input to the ESPM-T model so the heat transfer dynamics are not included. On board a vehicle, the cell temperature can be measured. In the simulated performance comparisons, the cell temperature is provided by the commercial code AutoLion-ST⁷⁰⁰ [17].

II. MATHEMATICAL MODELING

A. Governing Equations

In a Li ion cell during discharge, Li-ions deintercalate from the negative electrode

\[ \text{Li}_iC \xrightarrow{\text{discharge}} \text{C} + x\text{Li}^+ + xe^- \quad (1) \]

and intercalate into the positive electrode for LMO active material particles

\[ \text{Li}_{(1-x)}\text{MO}_2 + x\text{Li}^+ \xrightarrow{\text{discharge}} \text{LiMO}_2 \quad (2) \]
where M stands for a transition metal. The opposite reactions occur during charge.

The electrochemical model of a Li-ion cell can be described by four governing equations: Conservation of Li-ion \((Li^+)\) and conservation of charge \((e^-)\) in both the solid and electrolyte phases. Conservation of \(Li^+\) in a single, spherical, solid phase particle is described by Fick’s law of diffusion:

\[
\frac{\partial C_s}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_s}{\partial r} \right),
\]

where \(C_s(x,r,t)\), \(D_s\) is the diffusion coefficient, \(r\) is the radial distance from the particle center, and \(t\) is time. The model is valid for spherical and cylindrical geometry.

The boundary conditions of Eq. (6) are

\[
D_s \frac{\partial C_s}{\partial r} \Big|_{r=R_s} = -J_{li}/\alpha_s \Gamma_s,
\]

where \(J_{li} > 0\) for ion discharge and the interface surface area, \(\alpha_s = \frac{4\pi}{R_s}\). Conservation of \(Li^+\) in the electrolyte phase is governed by

\[
\varepsilon_e \frac{\partial C_e}{\partial t} = D_{eff} \frac{\partial^2 C_e}{\partial x^2} + \frac{1 - \varepsilon_s}{\varepsilon_e} \frac{J_{li}}{\alpha_s},
\]

where effective conductivity, \(\sigma_{eff} = \sigma \varepsilon_e\), and \(\sigma\) is the reference conductivity of the active material [1].

The lineardized electrolyte phase charge conservation equation [1], [6], [7]

\[
\kappa_{eff} \frac{\partial^2 \phi_e}{\partial x^2} + \frac{\kappa_{d}^0}{\sigma_{eff}} \frac{\partial^2 C_e}{\partial x^2} + J_{\text{li}} = 0
\]

has boundary conditions

\[
\left( \frac{\partial \phi_e^0}{\partial x} \right)_{x=0} = 0,
\]

\[
\left[ \left( \frac{\partial^2 \phi_e^0}{\partial x^2} \right) + \left( \kappa_{eff} \frac{\partial \phi_e^0}{\partial x} \right) \right]_{x=L_a} = \left[ \left( \frac{\partial^2 \phi_e^0}{\partial x^2} \right) + \left( \kappa_{eff} \frac{\partial \phi_e^0}{\partial x} \right) \right]_{x=L_{a+s}}.
\]

\[
\phi_e^0(L_a, t) = \phi_e^0(L_a, t),
\]

\[
\left( \frac{\partial^2 \phi_e^0}{\partial x^2} \right)_{x=L_a+L_s} = 0.
\]

The Bruggeman relation \(\kappa_{eff} = \kappa_e\) calculates the effective ionic conductivity. The effective diffusional conductivity

\[
\kappa_{d}^0 = \frac{2RT \kappa_{eff}^0}{F} \left( \frac{\varepsilon_s}{\varepsilon_e} - 1 \right) \left( 1 + \frac{\ln(\frac{R_s}{\varepsilon_s})}{\ln(\frac{R_s}{\varepsilon_e})} \right),
\]

according to concentrated solution theory. The Butler-Volmer (B-V) kinetic equation is

\[
j_{\text{li}} = a_i i_0 \left[ \exp \left( \frac{\alpha_a F \eta}{RT} \right) - \exp \left( \frac{\alpha_c F \eta}{RT} \right) \right].
\]

Overpotential

\[
\eta = \phi_s - \phi_e - U(c_{s,e}),
\]

drives the electrochemical reaction rate. The exchange current density is

\[
i_0(x, t) = k(T)c_{eff}^{ou} (c_{s,\text{max}} - c_{s,e})^{\alpha_a} c_{s,e}^{\alpha_c}.
\]

Finally, the cell voltage is

\[
V(t) = \phi_e^0(L_a, t) - \phi_e^0(0, t) - \frac{R_s}{A} i(t).
\]


B. Low Order Electrolyte Enhanced Single Particle Model (ESPM) Formulation

The assumption of the ESPM are: (i) infinite solid phase conductivity in the individual electrodes resulting no ohmic loss, (ii) uniform current distribution in the individual electrodes, (iii) linearized conservation equations in the electrolyte domain, and (iv) all properties evaluated at the equilibrium point (at 50% SOC). Assumptions (i), (ii), and (iv) are also used in SPM models.

Solid particle phase diffusion equation is solved by taking Laplace transform of Eq. (3) and applying the associated boundary conditions (Eqs. (4) - (5)) [18]. The final impedance transfer function at the particle surface of a spherical particle is

\[
\frac{\tilde{C}_{s,e}(s)}{\tilde{J}^L(s)} = \frac{1}{a_{1,F}} \left( \frac{R_n}{D_p} \right) \left[ \frac{\tanh(\beta)}{\tanh(\beta) - \beta} \right],
\]

where \( \beta = R_n \sqrt{s} \) and the tilde indicates a small perturbation from the equilibrium condition \( c_{s,e}^0(t) = \tilde{c}_{s,e}^0(t) \). Note that at equilibrium \( \tilde{c}, \tilde{J}, \) and \( \tilde{C} \) are zero, so tilde are unnecessary. Capital letters indicate a variable has been Laplace transformed.

Conservation of charge in the electrode (Eq. (13)) is simplified by integrating in each electrode domain and applying the boundary conditions (14) - (15). The final transfer functions are

\[
\frac{J^L_i(s)}{I(s)} = \frac{1}{AL_n}, \quad (29)
\]

\[
\frac{J^L_p(s)}{I(s)} = -\frac{1}{AL_p}, \quad (30)
\]

where the uniform current distributions are defined as \( J^L_i(s) = \frac{1}{t_p} \int_{L_n}^0 J^{L_i}(x,s)dx \) and \( J^L_p(s) = \frac{1}{L_n} \int_{0}^L J^{L_i}(x,s)dx \), in the positive and negative electrodes, respectively.

Substituting Eqs. (29) and (30) into Eq. (28) we get

\[
\frac{\tilde{C}_{s,e}^p(s)}{I(s)} = -\frac{1}{a_{1,F}AL_p} \left( \frac{R_p}{D_p} \right) \left[ \frac{\tanh(\beta^p)}{\tanh(\beta^p) - \beta^p} \right], \quad (31)
\]

\[
\frac{\tilde{C}_{s,e}^n(s)}{I(s)} = \frac{1}{a_{1,F}AL_n} \left( \frac{R_n}{D_n} \right) \left[ \frac{\tanh(\beta^n)}{\tanh(\beta^n) - \beta^n} \right], \quad (32)
\]

in the positive and negative electrodes, respectively. These transcendental transfer functions are infinitely differentiable and discretized using a Padé approximation [19], [20]. The 3rd order Padé approximations of Eqs. (31) and (32) are

\[
\frac{\tilde{C}_{s,e}^p(s)}{I(s)} = \frac{21}{s^3} \left[ \frac{x^2}{\alpha_{1,F} \alpha_{1,F} L_p} + \frac{600D_p^2}{\alpha_{1,F} \alpha_{1,F} R_n^2} + \frac{495D_p^2}{\alpha_{1,F} \alpha_{1,F} R_n^2} \right], \quad (33)
\]

\[
\frac{\tilde{C}_{s,e}^n(s)}{I(s)} = -\frac{21}{s^3} \left[ \frac{x^2}{\alpha_{1,F} \alpha_{1,F} L_n} + \frac{600D_n^2}{\alpha_{1,F} \alpha_{1,F} R_n^2} + \frac{495D_n^2}{\alpha_{1,F} \alpha_{1,F} R_n^2} \right], \quad (34)
\]

The linearized B-V Eq. (24) is

\[
\frac{\eta(s)}{\tilde{J}(s)} = \frac{R_{ct}}{a_s}, \quad (35)
\]

where the charge transfer resistance, \( R_{ct} = \frac{RT}{z_{1}(\alpha_{e} + \alpha_{c})F} \).

Combining Eqs. (29), (30), and (35),

\[
\frac{\eta_{p}(s)}{I(s)} = \frac{R_p}{a_p^2 AL_p}, \quad (36)
\]

\[
\frac{\eta_{n}(s)}{I(s)} = \frac{R_n}{a_n^2 AL_n}. \quad (37)
\]

Combining Eqs. (25) and (27) and linearizing around an equilibrium produces the voltage deviation in Laplace domain

\[
\frac{\tilde{V}(s)}{I(s)} = \frac{\eta_p(L,s)}{I(s)} - \frac{\eta_n(0,s)}{I(s)} + \Delta \phi_p(L,s) \frac{\tilde{C}_{s,e}^p(0,s)}{I(s)} - \frac{R_c}{A}. \quad (38)
\]

The open circuit potential (OCP) slopes \( \frac{\partial \tilde{V}_p}{\partial \tilde{C}_{s,e}^p} \) and \( \frac{\partial \tilde{V}_n}{\partial \tilde{C}_{s,e}^n} \) are evaluated at a specific SOC from the empirically measured open circuit potential functions [21], [22], [23].

Integral method analysis (IMA) [1], [14], [24], [25] is used to solve the Li-ion conservation Eq. (6) across the three domains of the cell. Substituting Eqs. (29) and (30) into the linearized Eq. (6) for the anode, separator and cathode give

\[
\varepsilon_{e,a} C^n_e(s) - D_n \frac{\partial^2 C^n_e(s)}{\partial x^2} \cdot b_1 I(s) = 0 \quad \text{for} \quad x \in (0, L_n), \quad (39)
\]

\[
\varepsilon_{e,s} C^n_e(s) - D_s \frac{\partial^2 C^n_e(s)}{\partial x^2} \cdot b_2 I(s) = 0 \quad \text{for} \quad x \in (L_n, L_n + L_s), \quad (40)
\]

\[
\varepsilon_{e,c} C^n_e(s) - D_p \frac{\partial^2 C^n_e(s)}{\partial x^2} \cdot b_3 I(s) = 0 \quad \text{for} \quad x \in (L_n + L_s, L), \quad (41)
\]

where \( b_1 = \frac{1}{FA_{La}} \), \( b_2 = \frac{1}{FA_L} \), and the superscript ‘eff’ on diffusivity has been removed for simplicity.

In the minimal IMA, the quadratic Li-ion concentration profiles in the individual domains are

\[
C^n_e(x,s) = c_{0,n}(s) + c_{1,n}(x)s + c_{2,n}(x)s^2, \quad (42)
\]

\[
C^n_e(x,s) = c_{0,s}(s) + c_{1,s}(x)s + c_{2,s}(x)s^2, \quad (43)
\]

\[
C^n_e(x,s) = c_{0,p}(s) + c_{1,p}(x)s + c_{2,p}(x)s^2, \quad (44)
\]

Note that Eqs. (42) - (44) are second order in \( x \) and third order in time domain. These quadratic distributions are substituted into Eqs. (39) - (41), integrated and applied with the associated boundary conditions (7) - (12) to obtain

\[
\frac{C^n_e(x,s)}{I(s)} = \frac{p_{2,n}(x)s^2 + p_{1,n}(x)s + p_{0,n}}{s(Q_{3,n} + Q_{2,n} + Q_{1,n})}, \quad (45)
\]

\[
\frac{C^n_e(x,s)}{I(s)} = \frac{p_{2,s}(x)s^2 + p_{1,s}(x)s + p_{0,s}}{s(Q_{3,s} + Q_{2,s} + Q_{1,s})}, \quad (46)
\]

\[
\frac{C^n_e(x,s)}{I(s)} = \frac{p_{2,p}(x)s^2 + p_{1,p}(x)s + p_{0,p}}{s(Q_{3,p} + Q_{2,p} + Q_{1,p})}. \quad (47)
\]
Coefficients \( p_0, \ldots, p_{2p} \) are not provided here due to space constraint. After substituting Eqs. (29) - (30) into Eq. (16), the electrolyte charge conservation equations in the three domains of the cell are

\[
\begin{align*}
\kappa_n \frac{\partial^2 \phi_n^p(s)}{\partial x^2} + \kappa_d, n \frac{\partial^2 \phi_n^p(s)}{\partial x^2} + b_3 I &= 0, \\
\kappa_d \frac{\partial^2 \phi_d^p(s)}{\partial x^2} + \kappa_d, d \frac{\partial^2 \phi_d^p(s)}{\partial x^2} &= 0, \\
\kappa_p \frac{\partial^2 \phi_p^p(s)}{\partial x^2} + \kappa_d, p \frac{\partial^2 \phi_p^p(s)}{\partial x^2} - b_4 I &= 0,
\end{align*}
\]

where \( b_3 = \frac{1}{\kappa_n}, b_4 = \frac{1}{\kappa_p}, \kappa_n = \frac{\kappa_{eff}}{e_{eff}}, \kappa_d, n = \frac{\kappa_{eff}}{e_{eff}}, \) and \( \kappa_d, d = \frac{\kappa_{eff}}{e_{eff}} \) for simplicity. Eqs. (48) - (50) and their associated boundary conditions, Eqs. (17) - (22), are singular due to the zero flux at \( x = 0 \) and \( x = L_a + L_s + L_p \). This situation can be avoided by defining electrolyte voltage difference relative to \( \phi_e(0, s) \) [1], [26].

Integrating Eqs. (48) - (50) spatially and subtracting \( \phi_n^p(0, s) \) give

\[
\begin{align*}
\kappa_n \Delta \Phi_n^p + \kappa_d, n [C_n^p(x, s) - C_n^p(0, s)] + \frac{b_3 I x^2}{2} &= C_{1n} x, \\
\kappa_d \Delta \Phi_d^p + \kappa_d, d [C_d^p(x, s) - \frac{\kappa_d, n}{\kappa_n} C_n^p(0, s)] &= C_{1d} x + C_{2d}, \\
\kappa_p \Delta \Phi_p^p + \kappa_d, p [C_p^p(x, s) - \frac{\kappa_p, d}{\kappa_n} C_n^p(0, s)] - \frac{b_4 I x^2}{2} &= C_{1p} x + C_{2p},
\end{align*}
\]

where \( C_{1n}, \ldots, C_{2p} \) are integration constants. Eqs. (51) - (53) are solved analytically using a similarly modified set of boundary conditions Eqs. (18) - (22) to give

\[
\Delta \Phi(L, s) = \frac{R_s s^2 + R_1 s + R_0}{L_2 s^2 + L_1 s + L_0}.
\]

The coefficients \( R_0, \ldots, R_2 \) are not provided in this paper due to space constraint. Eqs. (31), (32), (36), (37), and (38) are substituted into Eq. (38) to deduce the final ESPM impedance transfer function

\[
\frac{\bar{V}(s)}{I(s)} = K + \frac{K_1 + K_2}{s} + \frac{b_00 s^6 + b_01 s^5 + b_02 s^4 + b_03 s^3 + b_04 s^2 + b_05 s + b_06}{s^6 + a_01 s^5 + a_02 s^4 + a_03 s^3 + a_04 s^2 + a_05 s + a_06}.
\]

The simplification process and the coefficients \( a_{01}, \ldots, a_{06}, b_{00}, \ldots, b_{06}, K, K_1, \) and \( K_2 \) are described in Appendix A.

C. ESPM with Temperature Effect (ESPM-T)

For isothermal ESPM simulation at a particular temperature all the coefficients are constants and isism in MATLAB simulates the test response. For non-isothermal case (ESPM-T) the coefficients are updated with cell temperature obtained from AutoLion-STM output and simulated using ode45 from a state space realization of Eq. (55). For the NCM chemistry simulated in this paper, most significant temperature dependent parameters are solid phase diffusion coefficient, exchange current density, electrolyte diffusion coefficient, electrolyte ionic conductivity, and electrolyte diffusional ionic conductivity. Arrhenius equation

\[
\psi = \psi_{ref} \exp \left[ \frac{E_{act, \psi}}{R} \left( \frac{1}{T_{ref}} - \frac{1}{T} \right) \right],
\]

is used to calculate solid particle diffusion coefficient and exchange current density. The temperature dependent property \( \psi \) (e.g. \( D_s^p, D_e^p, \) and \( i_0 \)) depends on the reference value and the activation energy \( E_{act, \psi} \). The empirical correlations for electrolyte properties are extracted from Valøen et al. [27]:

\[
D_{e, l}(T) = \frac{4.43}{T} \left( \frac{51}{T - (229 + e_{e,0})} \right)^{0.22 e_{e,0}},
\]

\[
\kappa(T) = \exp \left[ -10.5 + 0.074 T - 6.96 \times 10^{-5} T^2 \right]
\]

\[
+ c_{e,0}(0.668 - 0.0178 T - 2.8 \times 10^{-5} T^2)
\]

TABLE I

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Neg. electrode</th>
<th>Separator</th>
<th>Pos. electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness, ( L ) (cm)</td>
<td>40 x 10^{-3}</td>
<td>25 x 10^{-3}</td>
<td>36.55 x 10^{-3}</td>
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<tr>
<td>Particle radius, ( R_s ) (cm)</td>
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<td>5 x 10^{-4}</td>
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<tr>
<td>Porosity (electrolyte phase volume fraction), ( \epsilon_e )</td>
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<td>0.4</td>
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<td>Maximum solid phase concentration, ( c_{e, \text{max}} ) (mol cm^{-3})</td>
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<td>51.83 x 10^{-3}</td>
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</tr>
<tr>
<td>Stoichiometry at 0%</td>
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<td>SOC, ( x_{SO_2}, \gamma_{SO_2} )</td>
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<td>Average electrolyte concentration, ( c_{e, 0} ) (mol cm^{-3})</td>
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<tr>
<td>Exchange current density, ( i_{0, ref} ) (A cm^{-2})</td>
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<td>2.0 x 10^{-3}</td>
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<td>Activation energy of ( i_0 ) (kJ mol^{-1})</td>
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<td>58</td>
<td></td>
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<td>Charge transfer coefficient, ( \alpha_n, \alpha_d )</td>
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<td>Li^+ transference number, ( \delta_0 )</td>
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<td>Solid phase Li diffusion coefficient, ( D_s^p (cm^2 s^{-1}) )</td>
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<td>Activation energy of ( D_s^p ) (kJ mol^{-1})</td>
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<tr>
<td>Contact resistance, ( R_c ) (\Omega cm^2)</td>
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</table>
\[
\kappa_{d,i} = -\frac{2RT \kappa_e^{eff}}{F} \left( t_i^+ - 1 \right) v(T),
\]

where \( \kappa_e^{eff} = \kappa_i(T) e_e^i \) for individual domains. The empirical correlation

\[
v(T) = 0.601 - 0.24 e_e^{0.5} + 0.982 [1 - 0.0052(T - 293)] c_e^{0.5},
\]

and \( i \) indicates an electrode domain.

### III. RESULTS AND DISCUSSION

#### A. Comparison of SPM and ESPM with AutoLion-ST\textsuperscript{TM} Under Isothermal Condition

In this work, EC Power’s AutoLion-ST\textsuperscript{TM} is considered to be the truth model and used to compare the accuracy of the reduced order SPM, ESPM, and ESPM-T. AutoLion-ST\textsuperscript{TM} is a 1+1D, fully non-linear, finite volume based model in MATLAB/ SIMULINK. It uses robust numerical algorithms to simulate electrochemical and thermal interactions of Li-ion batteries over a wide range of operating conditions [17].

Figures 1(a) - (c) compare the SPM, ESPM and AutoLion-ST\textsuperscript{TM} voltage responses at 25°C and 50% initial SOC corresponding to the pulse current input in Fig. 1(e). The zoomed in Fig. 1(a) shows that the SPM response deviates significantly from the ESPM and AutoLion-ST\textsuperscript{TM} voltage responses, even at lower C-rates. The ESPM voltage response, however, closely matches AutoLion-ST\textsuperscript{TM}, including 20°C - 10 sec pulses (see zoomed view in Fig. 1(b)).

Figure 1(d) shows the time response of the electrolyte potential \( \Delta \phi_e(t) = \phi_e(L,t) - \phi_e(0,t) \) is strongly C-rate dependent. This internal variable can not be predicted by ECMs. The ESPM, however, is based on the fundamental equations of the cell and internal variables such as \( \Delta \phi_e(t) \) can be predicted. The ESPM predicts electrolyte potential difference accurately at low C-rates but has almost 50% (314 mV) error at high C-rates. The quadratic concentration distributions and constant current distributions contribute into this error at higher C-rates. Although \( \Delta \phi_e(t) \) is underpredicted by the ESPM it is a significant improvement over SPM which neglects electrolyte dynamics entirely.

One can tune the SPM contact resistance to account for the unmodeled electrolyte dynamics. At higher C-rates, however, the SPM voltage response overshoots the AutoLion-ST\textsuperscript{TM} voltage response due to the neglect of electrolyte diffusion dynamics [11]. Although ESPM underpredicts \( \Delta \phi_e(t) \) at higher C-rates, the ESPM’s voltage matches the AutoLion-ST\textsuperscript{TM}’s voltage (see Fig. 1(b)). Overprediction of overpotentials resulting from the linearization of the B-V kinetic equation compensates for the underpredicted \( \Delta \phi_e(t) \). The maximum voltage error between the ESPM and AutoLion-ST\textsuperscript{TM} is 3% for the 20°C - 10 sec pulse.

#### B. Comparison of ESPM and ESPM-T with AutoLion-ST\textsuperscript{TM} Under Non-Isothermal Condition

Figure 2 shows the influence of cell initial temperature on the voltage response by comparing the simulation results from ESPM, ESPM-T, and AutoLion-ST\textsuperscript{TM}. Isothermal ESPM voltage response undershoots (Fig. 2(a)) and overshoots (Fig. 2(c)) at low and high temperatures, respectively, but matches very well around 25°C (Fig. 2(b)). This indicates the importance of incorporating the temperature effect into Li-ion cell models due to its inherent active nature. ESPM-T voltage response is in very good agreement at lower temperature and low C-rates (e.g. <1.5% at 2.5C discharge). The error increases at low temperatures and moderate C-rates (e.g. maximum 3.6% at 7.5C discharge), mainly attributed by the highly distributed currents along each electrode arising from sluggish reaction kinetics, reduced electrolyte diffusivity, and ionic conductivity at low temperatures. Note that, reducing the initial temperature further increases the relative voltage error (results not presented here). As the cell warms up the voltage error diminishes and results a good voltage match within 3.75% voltage error at 20°C - 10s discharge pulse at 50°C. Overall, ESPM-T matches AutoLion-ST\textsuperscript{TM} to within 3.75% for the entire 5°C - 50°C temperature range and up to 20C - 10s rates.
IV. CONCLUSIONS

The traditional SPM neglects electrolyte diffusion only provides satisfactory performance over narrow C-rate and temperature ranges. Using only seven states, the ESPM developed in this paper includes an IMA model of electrolyte diffusion and matches the AutoLion-STM pulse response up to 20°C at room temperature with 3% error. The ESPMT model updates the ESPM’s parameters with temperature and obtained a voltage response within 3.75% error at 50°C during 20°C - 10 sec charge-discharge pulses. The model’s performance away from the linearized point and the working range of ESPM-T in terms of C-rate and temperature will be reported in our future publications.

Appendix A: ESPM Impedance Transfer Function Derivation

Substituting Eqs. (33), (34), (36), (37), and (54) into Eq. (38) we obtain,

\[
\tilde{Y}(s) \frac{I(s)}{V(s)} = K + \frac{R_{s2}s^2 + R_{i2}s + R_0}{L_2s^2 + L_1s + L_0} + \frac{\alpha_1^2s^2 + 60\alpha_1\alpha_2s + 495\alpha_1\alpha_2^2}{s^2 + 189\alpha_1\alpha_2^2 + 3465\alpha_2^2} + \frac{\beta_1s^2 + 60\beta_1\beta_2s + 495\beta_1\beta_2^2}{s^2 + 189\beta_1\beta_2^2 + 3465\beta_2^2},
\]

where,

\[
K = \left(-\frac{R_0}{L_0} + \frac{R_{s1}}{L_1} + \frac{R_{i2}}{L_2}\right), \quad C_0 = 2\left(\frac{\alpha_{s1}}{\alpha_{i2}}\right), \quad \alpha_1 = \frac{\alpha_{s1}}{\alpha}, \quad \alpha_2 = \frac{\alpha_{i2}}{\alpha}, \quad \beta_1 = \frac{\beta_{s1}}{\beta}, \quad \beta_2 = \frac{\beta_{i2}}{\beta},
\]

Simplifying Eq. (A.1)

\[
\tilde{Y}(s) \frac{I(s)}{V(s)} = K + \frac{E_0s^2 + E_1s + E_2}{s^2 + F_1s + F_2} + \frac{A_2s^2 + A_1s + A_0}{s^2 + B_2s + B_1} + \frac{C_2s^2 + C_1s + C_0}{s^2 + D_2s + D_1},
\]

Factoring out one integrator, Eq. (A.2) can be written as:

\[
\tilde{Y}(s) \frac{I(s)}{V(s)} = K + \frac{K_1 + K_2}{s} + \frac{E_0s^2 + E_1s + E_2}{s^2 + F_1s + F_2} + \frac{g_1s^3 + g_2s^2 + g_3s + g_4}{s^2 + h_1s^2 + h_2s + h_3s + h_4},
\]

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REFERENCES


\[
b_{03} = g_3 + E_0h_3 + E_1h_2 + E_2h_1 + F_1g_2 + F_2g_1,
\]

\[
b_{01} = g_4 + E_0h_4 + E_1h_3 + E_2h_2 + F_1g_3 + F_2g_2,
\]

\[
b_{05} = E_1h_4 + E_2h_3 + F_1g_4 + F_2g_3 + h_06 = E_2h_4 + F_2g_4,
\]

\[
a_{01} = F_1 + h_1, a_{02} = F_2 + h_2 + F_1h_1,
\]

\[
a_{03} = F_2h_2 + F_1h_1, a_{04} = h_3 + F_1h_2 + F_2h_1,
\]

\[
a_{05} = F_1h_4 + F_2h_3, a_{06} = F_2h_4.
\]