A Composite Single Particle Lithium-ion Battery Model through System Identification

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Abstract—In the realm of Lithium-ion (Li-ion) battery modeling, owing to its simplicity, the Single Particle Model (SPM) has long been considered to be a promising Reduced Order Model (ROM) candidate to usher in the era of Physics-Inspired Models (PIMs) in embedded applications. However, at high load currents, the standard SPM exhibits poor accuracies in computing the cell's terminal voltage, thereby rendering it unsuitable as the plant model in state-estimation tasks. A comprehensive evaluation of the salient electrolyte-enhanced SPMs from literature reveals that current solutions are either mathematically intractable or overly simplistic. For the ionic concentration in the electrolyte, the well-known quadratic approximation model, which straddles the boundary of computational complexity and mathematical tractability, reveals a poor temporal performance, particularly at the current collector interfaces. In this work, we retain the spatial dynamics of the quadratic approximation model, whilst proposing a novel approach using system identification techniques for its temporal dynamics. By employing linear approximations for the relevant subsystems, we identify discrete-time transfer functions of the de-biased number of moles per unit area of lithium ions in the electrolyte within each electrode region, yielding improved spatio-temporal accuracies for the electrolyte concentration profile. We then augment the standard SPM with the new system identification-based electrolyte dynamics to arrive at an Electrolyte-Enhanced Composite Single Particle Model (EECSPM). Finally, we demonstrate superior performance of the EECSPM when compared with the incumbent state-of-the-art, thereby representing a concrete advancement towards the goal of using PIMs in real-time applications.

Index Terms—Lithium-ion batteries, System identification, Reduced order systems, Battery management systems, Linear systems, Mathematical model, Transfer functions.

NOMENCLATURE

A. Roman

$(\bar{c}_s), c_s$	(Bulk) concentration of Li^0 in the electrode (mol/m^3). (Bulk) concentration of Li^0 in the electrode (mol/m^3).
$c_{s,\text{surf}}$	Concentration of Li^0 at electrode surface (mol/m^3). Concentration of Li^0 at electrode surface (mol/m^3).
D_s	Intrinsic diffusivity of electrode (m^2/s). Intrinsic diffusivity of electrode (m^2/s).

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$\bar{q}$	Volume averaged concentration flux in the electrode along the radial position r ($\text{mol}/(\text{m}^2 \text{s})$). Volume averaged concentration flux in the electrode along the radial position r ($\text{mol}/(\text{m}^2 \text{s})$).
V_{cell}	Terminal voltage of the cell (V). Terminal voltage of the cell (V).
z	State of charge of the cell. State of charge of the cell.
<i>B. Greek</i>	
α	Charge transfer coefficient of the electrode. Charge transfer coefficient of the electrode.
η	Electrode overpotential (V). Electrode overpotential (V).
$\kappa/\kappa_{\text{eff}}$	Intrinsic/effective electrolyte conductivity (S/m). Intrinsic/effective electrolyte conductivity (S/m).
ϕ_s/ϕ_e	Electric potential in the electrode/electrolyte (V). Electric potential in the electrode/electrolyte (V).
θ	Surface stoichiometry of the electrode. Surface stoichiometry of the electrode.

I. INTRODUCTION

THE burgeoning demand for clean energy has driven the exploration of advanced methods of energy storage [1]. However, with this surge in demand comes stricter requirements for their longevity, performance, and adhesion to safety requirements, particularly for adoption in mainstream transport electrification [2]. In contrast to other incumbent technologies, Lithium-ion (Li-ion) batteries have several advantages such as high energy density, long life-cycles, low internal resistance, low self-discharge, fast charge and discharge cycles [3], [4]. This makes them the preferred choice energy storage and on-demand retrieval in modern consumer electronics and Battery Electric/Plug-in Hybrid Electric Vehicles (xEVs).

Through accurate model representations of their characteristics, advanced monitoring and control strategies can be deployed for increasing the cycle-life, improving the operational safety and performance of Li-ion batteries [4]. This has led to research efforts in constructing models of the electrochemical and system-level performance of Li-ion cells with varying levels of sophistication [5], [6]. The need to address operational challenges of Li-ion cells in an embedded environment such as on-board an electric vehicle has led to an increased impetus on developing advanced Battery Management Systems (BMSs). The only measurable quantities of a Li-ion cell are its terminal voltage, current and temperature. This implies that several

internal states of the cell such as its State of Charge (SOC) need to be estimated from these available measurements. Therefore, the performance of a BMS in such online state estimation tasks depends upon the fidelity of the underlying cell model. Sophisticated cell models enable these quantities to be estimated more accurately and facilitate the implementation of advanced control algorithms. Therefore, it is imperative that the cell model used is suitable for being embedded in a real-time BMS.

Physics-Based Models (PBMs) consist of governing equations that describe the cell's behavior based upon principles such as equilibrium thermodynamics, material diffusion and reaction kinetics. PBMs can facilitate the computation of the cell's internal physical quantities for arbitrary current inputs. The model's computations e.g., lithium concentration at electrode surfaces, can help in designing strategies to prevent plating-induced degradation [7]–[10]. The Doyle-Fuller-Newman (DFN) model, a well-known PBM, is briefly discussed in section I-A.

A. The Doyle-Fuller-Newman (DFN) model

The DFN model of a Li-ion cell describes the time evolution of the electric potentials and material/ion concentrations of the solid and electrolyte phases in addition to the molar flux density at the solid-electrolyte boundary [11], [12].

Taking cognizance of the fact that the reaction/diffusion dynamics along the shortest axial path dominates over that across the planar cross-section, a standard numerical implementation of the DFN dynamics is the Pseudo Two-Dimensional (P2D) model, where all field variables are computed at spatial nodes located along the cell's axial thickness. The solid concentration in spherical electrode particles is solved in a radial co-ordinate system (pseudo-dimension) perpendicular to the axial thickness. The axial and radial dimensions are coupled at the particle surface through the interfacial molar flux density j i.e., the rate of pore-wall flux crossing the electrode-electrolyte interface.

A major disadvantage of the P2D model is its computational complexity and hence, are not typically suitable for embedded applications. Nonetheless, for high performance applications such as in automotive BMSs there is an overwhelming demand for obtaining insight into internal cell variables. In view of this consideration, model order reduction techniques play a key role in porting a relevant subset of the P2D model onto a real-time microcontroller [13]–[16]. Owing to its simplicity, the Single Particle Model (SPM) is a promising Reduced Order Model (ROM) candidate with the potential to usher in the era of PBMs in embedded applications, and is summarized in section I-B.

B. The Single Particle Model (SPM)

To establish the context for our work, we present a brief summary of the SPM from literature [7], [17]–[20]. In the SPM, the negative and positive electrodes of the cell are idealized as spheres. Hence, the lithium concentration within each electrode is only a function of the radial position. Each sphere's surface area is scaled to be equivalent to the active area of the corresponding porous electrode. Solid phase diffusion is typically solved using polynomial approximation [21], [22]. The SPM thus employs the coarsest possible spatial discretization to minimize computational burden.

The basic SPM attributes the cell's voltage polarization to two dominant dynamics *viz.* reaction kinetics and solid phase diffusion. This stems from the assumption that charge transfer happens throughout the surface of each representative spherical particle where intercalation occurs. The electronic conductivity of the solid phase is assumed to be high such that the local volumetric current density is uniform along the thickness of each porous electrode. Solid phase diffusion dynamics are governed by concentration gradients induced due to pore-wall flux density at their surfaces. This interfacial flux is driven by a constant averaged electrochemical reaction rate. The model considers instantaneous charge transport between electrodes through the electrolyte, by assuming that electrolytic diffusion is significantly faster than solid diffusion. Thus, mass transport in the electrolyte is neglected. The electrolyte concentration is assumed to be constant at its equilibrium initial value. Hence, in the basic SPM, the electrolyte dynamics do not affect the cell's terminal voltage.

(1)–(3) represent the digested mathematical summary of the SPM obtained using the aforementioned assumptions, whose detailed derivations are discussed in the literature [7], [17]–[20].

$$\frac{d}{dt} \bar{q}_\lambda = -30 \frac{D_{s,\lambda}}{R_{p,\lambda}^2} - \frac{45}{2} \frac{j_\lambda}{R_{p,\lambda}^2}; \quad \bar{q}_\lambda(0) = 0, \quad (1)$$

$$\frac{d}{dt} \bar{c}_{s,p} = \frac{-3j_p}{R_{p,p}}; \quad \bar{c}_{s,p}(0) = f(z_0) \text{ analogous to (3f)} \quad (2)$$

$$V_{\text{cell}} = \eta_p - \eta_n + U_p - U_n \quad (3)$$

$$\eta_\lambda = \frac{2RT}{F} \sinh^{-1} \left(\frac{j_\lambda}{\mathcal{J}_\lambda(c_{e,0})} \right); \quad \alpha_\lambda = 0.5 \quad (3a)$$

$$U_\lambda = \mathcal{U}_\lambda(\theta_\lambda), \quad \theta_\lambda = \frac{c_{s,\text{surf},\lambda}}{c_{s,\text{max},\lambda}}, \quad j_\lambda = \frac{\mp I}{A l_\lambda a_{s,\lambda} F} \quad (3b)$$

$$\mathcal{J}_\lambda = 2k_\lambda \sqrt{c_{e,0} c_{s,\text{surf},\lambda} (c_{s,\text{max},\lambda} - c_{s,\text{surf},\lambda})} \quad (3c)$$

$$c_{s,\text{surf},\lambda} = \bar{c}_{s,\lambda} + \frac{8R_{p,\lambda}}{35} \bar{q}_\lambda - \frac{R_{p,\lambda}}{35D_{s,\lambda}} j_\lambda \quad (3d)$$

$$z = \frac{\frac{\bar{c}_{s,p}}{c_{s,\text{max},p}} - \theta_{0\%p}}{\theta_{100\%p} - \theta_{0\%p}} \quad (3e)$$

$$\bar{c}_{s,n} = c_{s,\text{max},n} \left[z (\theta_{0\%n} - \theta_{100\%n}) + \theta_{0\%n} \right] \quad (3f)$$

where $I > 0$ represents *discharge* currents and $\lambda \in \{n, p\}$. Herein, we have assumed a quadratic polynomial approximation model for solving solid phase diffusion. This is not intrinsic to the SPM, but has been applied to efficiently solve the governing equations.

The set of Ordinary Differential Equations (ODEs) given by (1), (2) can be simulated as a standard Initial Value Problem (IVP) yielding the mean lithium concentration in the electrodes. This is used to directly compute the cell's SOC (3e) and feeds into the sequence of calculations yielding its terminal voltage (3).

The basic SPM suffers from poor voltage accuracies even at moderate C-rates. This renders the model unsuitable for observer design in SOC estimation applications. Recent research efforts have aimed to mitigate this drawback through inclusion of electrolyte dynamics and are briefly discussed in section I-C.

C. Drawbacks of state-of-the-art in electrolyte enhanced SPMs

Our work was motivated by the need to address the drawbacks observed in our analysis of the current state-of-the-art in

electrolyte-enhanced SPMs, particularly in the context of their suitability for embedded implementation.

Di Domenico *et al.* presented a step-by-step derivation of the approximate analytical solution to the electrolyte overpotential [20]. The potential drop in the electrolyte is given by (4).

$$\phi_{e_p} - \phi_{e_n} = -\frac{I}{2A} \left(\frac{l_n}{\kappa_{eff_n}} + \frac{2l_s}{\kappa_{eff_s}} + \frac{l_p}{\kappa_{eff_p}} \right) \quad (4)$$

Equation (4) represents only a part of the electrolyte overpotential since the mass transport effects in the electrolyte have not been accounted for. Furthermore, results of applying dynamic current profiles were not presented. Hence, this model cannot be viewed as a *sufficient* enhancement to the basic SPM.

The terms representing electrolyte overpotentials owing to ionic concentration gradients within the cell thickness was explored by Prada *et al.* [23]. Thus, (4) gets modified as

$$\phi_{e_p} - \phi_{e_n} = (1 - t_+^0) \frac{2RT}{F} \ln \frac{c_{e_p/cc}}{c_{e_n/cc}} - \frac{I}{2A} \left(\frac{l_n}{\kappa_{eff_n}} + \frac{2l_s}{\kappa_{eff_s}} + \frac{l_p}{\kappa_{eff_p}} \right) \quad (5)$$

However these authors do not quantify the spatio-temporal evolution of ionic concentration at the current collector interfaces which influence the cell's voltage. Nevertheless, the aforesaid work is a noteworthy contribution and (5) can be used once the ionic concentrations have been computed.

Rahimian *et al.* provided approximate expressions for *both* charge transport and mass transport properties of the electrolyte [24]. A cubic polynomial approximation was used within the porous electrodes, whose coefficients were obtained by iteratively solving a large coupled system of algebraic equations, embedding within them the additional equations evaluated at some interior points. An online numerical optimization was performed to obtain the optimal placement of the interior nodes. A notable omission in the aforesaid work is the discussion of the model's performance to dynamic input profiles.

Luo *et al.* derived a parabolic approximation of the electrolyte concentration along the thickness of the cell [25]. Subsequently, a similar approach was adopted for the electrolyte potential to arrive at an extended SPM. The derivations were performed primarily for the steady-state with an extension for dynamic operating conditions by introducing two exponential scaling functions. The computation of certain time-constants used and the steps to obtain these scaling functions were not elucidated.

Tanim *et al.* accounted for electrolyte dynamics by deriving transfer functions for ionic concentration distribution and electrolyte overpotential using the Integral Method Approximation (IMA) technique [26]. However, the coefficients of these transfer functions were excessively long and comprised of chained algebraic operations expressed in a high-entropy sum-of-products form. Ten coefficients were needed to describe the concentration profile while six were required for the electrolyte potential. The median length of each atomic sub-expression was so high that they obfuscate their physical significance, whilst also rendering them error-prone for numerical implementation.

Moura *et al.* proposed an improved SPM by augmenting the conventional SPM with a simplified form of electrolyte-specific equations of the original DFN model [27]. The resulting model therefore has Partial Differential Equations (PDEs) in it and are therefore not amenable for embedded implementation.

Fig. 1. Schematic diagram of a Li-ion cell showing the co-ordinate systems of the quadratic approximation model of electrolyte concentration profile. The global spatial co-ordinate is $x \in \{0, l_{tot}\}$, where $l_{tot} = l_n + l_s + l_p$. Three local co-ordinate systems z are also defined.

Lotfi *et al.* presented an algebraic approximation for the spatial distribution of electrolyte concentration by modifying standard parabolic expressions with leading exponential coefficients [28]. The resulting set of equations were non-linear, which poses difficulties in the context of embedded implementation.

Han *et al.* proposed an extended SPM wherein the ionic spatial concentration was approximated by a parabolic concentration profile which exhibits good spatial accuracy [29]. However, the model's performance for the *transient* phase at the current collector interfaces for the constant current discharge case was not studied. Examining the static plots presented therein, it is clear that the errors during transient phase are higher than the steady state errors. However, the aforesaid work does not discuss or propose a mitigation strategy for the mediocre temporal performance of their model at the current collector interfaces prior to reaching steady-state. The ionic concentration profile for dynamic inputs were also not studied. Owing to its simplicity and spatial accuracy, the aforementioned semi-empirical Physics-Inspired Model (PIM) (henceforth referred to as the 'quadratic approximation' model) is amenable for embedded implementation and warrants our investigation reported herein.

The rest of the paper is organized as follows. In section II, we first provide a digested summary of the quadratic approximation model and present simulation studies with constant current and dynamic inputs. The sub-optimal temporal performance of the quadratic model's electrolyte concentration profile, particularly at the current collectors, motivates our research towards mitigation this drawback. In section III, we decouple the spatial and temporal electrolyte subsystems and whilst retaining the quadratic spatial profile, propose a high-fidelity replacement for the temporal subsystem through the application of system identification techniques, whose performance is evaluated in section IV. Upon obtaining an improved ionic concentration model, we use it to compute the overall electrolyte overpotential and augment the standard SPM with the electrolyte dynamics to arrive at an Electrolyte-Enhanced Composite Single Particle Model (EECSPM) in section V. In section VI, we demonstrate the improved performance of our proposed EECSPM to that of the quadratic approximation model, with the P2D model as a reference benchmark. Finally, section VII highlights the salient conclusions drawn from our findings and paves the way for future research by identifying key unsolved tasks in using physics-inspired ROMs for such embedded applications.

II. PERFORMANCE EVALUATION OF THE QUADRATIC APPROXIMATION MODEL

A. Mathematical Background

We first summarize the governing equations of the quadratic approximation model from literature [29], [33]. Our proposed modeling improvements discussed in section III relies upon this mathematical background. Fig. 1 shows the co-ordinate definitions in the governing equations of the quadratic approximation model of ionic concentration in the electrolyte. The globally defined x co-ordinate starts at the negative current collector interface ($x = 0$) and terminates at the positive current collector interface ($x = l_{\text{tot}}$, where $l_{\text{tot}} = l_n + l_s + l_p$). Three local co-ordinate systems (each denoted by z) have also been defined.

Quadratic expressions are used for approximating the electrolyte concentration profile within each cell region.

$$c_{e,n}(z, t) = a_2(t)z^2 + a_1(t)z + a_0(t) \quad 0 \leq z \leq l_n \quad (10)$$

$$c_{e,s}(z, t) = a_5(t)z^2 + a_4(t)z + a_3(t) \quad 0 \leq z \leq l_s \quad (11)$$

$$c_{e,p}(z, t) = a_8(t)z^2 + a_7(t)z + a_6(t) \quad 0 \leq z \leq l_p \quad (12)$$

where the coefficient vector $\vec{a}(t) = [a_0(t) \ a_1(t) \ \dots \ a_8(t)]$ is to be determined. By applying the pertinent electrolyte-specific boundary conditions of the DFN model and through a series of subsequent mathematical transformations (see Deng *et al.* [33]), we obtain the set of Differential Algebraic Equations (DAEs) (13)–(23) describing the quadratic approximation spatio-temporal model of ionic concentration.

$$a_2 l_n^2 + a_0 = a_3 \quad (\text{continuity at neg/sep interface}) \quad (13)$$

$$a_5 l_s^2 + a_4 l_s + a_3 = a_8 l_p^2 + a_6 \quad (\text{continuity at sep/pos interface}) \quad (14)$$

$$2a_2 l_n D_{\text{eff},n} = a_4 D_{\text{eff},s} \quad (\text{flux b.c. at neg/sep interface}) \quad (15)$$

$$(2a_5 l_s + a_4) D_{\text{eff},s} = -2a_8 l_p D_{\text{eff},p} \quad (\text{flux b.c. at sep/pos interface}) \quad (16)$$

$$Q_{e,n} = \varepsilon_n \left(\frac{1}{3} a_2 l_n^3 + a_0 l_n \right) \quad (17)$$

$$Q_{e,s} = \varepsilon_s \left(\frac{1}{3} a_5 l_s^3 + \frac{1}{2} a_4 l_s^2 + a_3 l_s \right) \quad (18)$$

$$Q_{e,p} = \varepsilon_p \left(\frac{1}{3} a_8 l_p^3 + a_6 l_p \right) \quad (19)$$

$$\frac{d}{dt} Q_{e,n} = 2a_2 l_n D_{\text{eff},n} + (1 - t_+^0) \frac{I}{AF}; \quad Q_{e,n}(0) = \varepsilon_n c_{e,0} l_n \quad (20)$$

$$\frac{d}{dt} Q_{e,s} = 2a_5 l_s D_{\text{eff},s}; \quad Q_{e,s}(0) = \varepsilon_s c_{e,0} l_s \quad (21)$$

$$\frac{d}{dt} Q_{e,p} = 2a_8 l_p D_{\text{eff},p} - (1 - t_+^0) \frac{I}{AF}; \quad Q_{e,p}(0) = \varepsilon_p c_{e,0} l_p \quad (22)$$

$$\vec{a}(0) = [c_{e,0} \ 0 \ c_{e,0} \ 0 \ 0 \ c_{e,0} \ 0] \quad (23)$$

$Q_{e,j}$ denote the number of moles of Li^+ in the electrolyte per unit cross-sectional area within each cell region $j \in \{n, s, p\}$.

B. Simulation-based analysis of quadratic approximation model

In this section, we discuss the performance of the quadratic approximation model through simulation and by comparing it against a benchmark model incorporating the full P2D dynamics.

Table I lists the electrochemical, geometric, kinetic and transport properties of a Lithium Cobalt Oxide (LCO) cell which we used in our simulations. For the P2D model, we used v2.0 of the LIONSIMBA toolbox [35] which has been widely applied for such benchmarking purposes in battery modeling literature [32],

[36]–[39]. Table II lists the conditions pertaining to numerical simulation of the models discussed in this work.

Fig. 2 shows simulation results for a 1C discharge current, wherein the spatial distribution of Li^+ ions in electrolyte along the cell's thickness obtained from the P2D and quadratic approximation models are plotted at various snapshots of time. The concentration profile within each electrode region exhibits a characteristic inflection point during the transient phase for which the quadratic approximation model exhibits a large percentage error. However, as we advance in time, this inflection point flattens out and the quadratic model's output becomes closer to the true concentration values.

Fig. 3 shows the time evolution of electrolytic concentration at the two current collector interfaces. At the negative current col-

Fig. 2. Spatial distribution of ionic concentration in the electrolyte along cell thickness at various snapshots of time for a 1C discharge. With the output of the P2D model as the reference, the quadratic approximation model exhibits large errors during the initial transient duration, but improves over time.

Fig. 3. Time evolution of ionic concentration in the electrolyte at the two current collector interfaces for a 1C discharge (top row) as computed by the P2D and quadratic approximation models. The time evolution of the error in the output of the quadratic approximation model (with respect to the P2D model) at the two current collectors is shown in the bottom row of plots.

TABLE I

THERMODYNAMIC, KINETIC, GEOMETRIC AND TRANSPORT PROPERTIES OF THE CHOSEN LITHIUM COBALT OXIDE (LCO) CELL. THE HIGHLIGHTED ENTRIES REPRESENT THOSE PARAMETERS THAT ARE EXCLUSIVE TO THE P2D MODEL. $j \in \{p, s, n\}$.

Parameter	Pos	Sep	Neg
Intrinsic electrolyte conductivity (P2D), κ_{jP2D} (S/m)	—	see (6)	—
Intrinsic electrolyte diffusivity (P2D), D_{jP2D} (m ² /s)	—	see (7)	—
Intrinsic electronic conductivity, σ_j (S/m)	^a 100.00	—	^a 100.00
Li ⁺ transference number, t_+^0	^a 0.363	^a 0.363	^a 0.363
Particle radius, R_{p_j} (m)	^a 2×10^{-6}	—	^a 2×10^{-6}
Electrolyte volume fraction, ε_j	^a 0.385	^a 0.724	^a 0.485
Filler vol. fraction, ε_{fj}	^a 0.025	—	^a 0.033
Electrode diffusivity, D_{s_j} (m ² /s)	^a 1×10^{-14}	—	^a 3.9×10^{-14}
Bruggeman coefficient, brugg_j	^a 4	^a 4	^a 4
Max concentration, $c_{s,\max_j}$ (mol/m ³)	^a 51 554	—	^a 30 555
Reaction rate coefficient, k_{r_j} (m ^{2.5} mol ^{-0.5} /s)	^a 2.33×10^{-11}	—	^a 5.03×10^{-11}
Surface stoichiometry at 100 % cell SOC, $\theta_{\max_j}$	^a 0.4955	—	^a 0.8551
Surface stoichiometry at 0 % cell SOC, $\theta_{\min_j}$	^b 0.9917	—	^b 0.0143
Thickness, l_j (m)	^a 72×10^{-6}	^a 25×10^{-6}	^b 88×10^{-6}
Overall active surface area, A (m ²)	^b 2.053	—	^b 2.053
Specific interfacial surface area, a_{s_j} (m ² /m ³)	^c 885×10^3	—	^c 723.6×10^3
Intrinsic electrolyte conductivity (ROMs), κ_{jROMs} (S/m)	^d 1.2×10^{-4}	—	^d 1.2×10^{-4}
Intrinsic electrolyte diffusivity (ROMs), D_{jROMs} (m ² /s)	^e 3.22×10^{-10}	^e 3.22×10^{-10}	^e 3.22×10^{-10}
Open circuit potential, $\mathcal{U}_j$ (V)	see table note <i>f</i>	—	see table note <i>g</i>

$$\kappa_j(c_e(x, t), T) = 10^{-4} \times c_e(x, t) \left(-10.5 + 0.668 \times 10^{-3} c_e(x, t) + 0.494 \times 10^{-6} c_e^2(x, t) + (0.074 - 1.78 \times 10^{-5}) c_e(x, t) - 8.86 \times 10^{-10} c_e^2(x, t) \right) T + (-6.96 \times 10^{-5} + 2.8 \times 10^{-8} c_e(x, t) T^2)^2 \quad \text{using coefficients from table III of Ref. [30]} \quad (6)$$

$$D(c_e, T) = 10^{-4} \times 10^{-4.43 - \frac{54}{T(t) - 229.5 \times 10^{-3} c_e(x, t)}} - 0.22 \times 10^{-3} c_e(x, t) \quad \text{using coefficients from table II of Ref. [30]} \quad (7)$$

$$^a \text{Ref. [31]} \quad ^b \text{Ref. [32]} \quad ^c \text{Computed as } a_{s_j} = \frac{3\varepsilon_{s_j}}{R_{p_j}}, j \in \{n, p\}$$

$$^d \text{By evaluating (7) at } T_{\text{cell}} = 298.15 \text{ K and } c_{e,0} = 1000 \text{ mol/m}^3 \quad ^e \text{By evaluating (6) at } T_{\text{cell}} = 298.15 \text{ K and } c_{e,0} = 1000 \text{ mol/m}^3$$

$$^f \mathcal{U}(\theta_p) = \frac{-4.656 + 88.669\theta_p^2 - 401.119\theta_p^4 + 342.909\theta_p^6 - 462.471\theta_p^8 + 433.434\theta_p^{10}}{-1 + 18.933\theta_p^2 - 79.532\theta_p^4 + 37.311\theta_p^6 - 73.083\theta_p^8 + 95.96\theta_p^{10}} \quad (8)$$

$$^g \mathcal{U}(\theta_n) = 0.7222 + 0.1387\theta_n + 0.029\theta_n^{0.5} - \frac{0.0172}{\theta_n} + \frac{0.0019}{\theta_n^{1.5}} + 0.2808 e^{(0.9-1.5\theta_n)} - 0.7984 e^{(0.4465\theta_n-0.4108)} \quad (9)$$

TABLE II

SETUP CONDITIONS FOR NUMERICAL SIMULATION OF THE LITHIUM COBALT OXIDE (LCO) CELL PARAMETERIZED IN TABLE I. THE HIGHLIGHTED ENTRIES ARE EXCLUSIVE TO THE P2D MODEL.

Parameter	Value
Nodes in through-thickness (axial), N_{a_j} , $j \in \{n, s, p\}$	^a 15
Nodes within spherical particle (radial), N_{r_j} , $j \in \{n, p\}$	^a 10
Cell temperature, T_{cell} (K)	^b 298.15
Initial electrolyte concentration, $c_{e,0}$ (mol/m ³)	^b 1000
Faraday constant, F (C/mol)	96487
Universal gas constant, R (J/(mol K))	8.314

^a Ref. [32] ^b Ref. [34]

lector interface, the concentration exhibits some low-amplitude oscillations owing to the complex interactions of the ionic phase with the porous electrode and the charge transfer process at the electrode-electrolyte boundary. The quadratic model's output is unable to capture this intricate time-evolution pattern since its temporal governing equation is the *first-order* ODE of (20) (with a proportional mapping from $Q_{e,n}$ to $c_e(0, t)$). The step response of a classical first order ODE is an exponential rise approaching a final settling value, which aligns with the simulation output (top-left plot). The ionic concentration evolution at the positive

current collector does not exhibit major oscillations and even has a subtle monotonicity to its response. Despite this, the first order response of the model fails to track its dynamics. The errors at both current collector interfaces are of similar magnitude, with a maximum absolute error of $\approx 250 \text{ mol/m}^3$.

In our analysis, the weakness of the quadratic approach lies in the fact that, unlike the spatial algebraic equations which have continuity and flux boundary conditions at the two separator interfaces, there is no equality constraint on the spatial derivatives computed symbolically from the assumed 2nd order polynomial expressions of (10)–(12) to obtain the RHS of the ODEs (20)–(22), which are therefore free to evolve without bounds. To address this, in section III we propose a system identification approach for its temporal subsystems.

III. A NEW ELECTROLYTE CONCENTRATION MODEL THROUGH SYSTEM IDENTIFICATION

A. Selection of methodology — background and rationale

The quadratic approximation model shows that pre-assuming a simplified structure for the final model equations and adapting its coefficients to physical constraints, yields a potentially viable candidate for describing electrolyte dynamics for later inclusion in the conventional SPM. From (5), we see that the ionic

Fig. 4. Input current profiles used as the training (Fig. 4a) and validation (Fig. 4b) inputs for system identification. The training sequence consists of *a*) a Random Binary Signal (RBS), *b*) a ‘chirp’ (swept cosine) signal (0–100 mHz), and *c*) a Periodic Random Binary Signal. The validation sequence consists of *a*) a Random Gaussian Signal (RGS), *b*) a Pseudorandom Binary Signal (PRBS), and *c*) a multisine waveform with fundamental frequencies from 100 mHz up to the Nyquist frequency. These sequences have been designed to cover a wide frequency range incorporating the potential to excite the salient modes of the system to be identified.

concentration has both direct and indirect contributions to electrolyte overpotential. Hence, we focus on obtaining suitable alternative expressions for the *time evolution* of electrolyte concentration whilst retaining the quadratic approach for describing its spatial profile. This approach of spatio-temporal decoupling is motivated by the observation that the quadratic model has a natural ‘pause’ in its model description. To clarify, (13)–(19) form a tightly coupled ‘square’ system i.e., seven linear equations with as many unknowns. However, the time evolution of $Q_{e,j}$ are described by first order ODEs given by (20)–(22).

In embedded implementations, it is prudent to solve the ODEs in a decoupled manner i.e., using coefficients of the linear system solution (13)–(19) from the previous time-step. We hypothesized that by taking advantage of the natural break in this operational sequence, it ought to be possible to break the coupling between the spatial derivative of concentration and its time-evolution counterpart. This served as our motivation to replace the underperforming time-evolution ODEs of the quadratic model with a superior alternative through black box system identification.

B. Electrolyte temporal subsystems and persistent excitations

$Q_{e,j}$ denote moles of Li^+ per cross-sectional area within each cell region. We seek to obtain two transfer functions of $Q_{e,n}$ and $Q_{e,p}$ to the applied current I in the frequency domain i.e., $\frac{Q_{e,n}(s)}{I(s)}$ and $\frac{Q_{e,p}(s)}{I(s)}$. In this work, these transfer functions shall be obtained for the P2D model which is considered to be representative of a real cell. Since the total moles of Li^+ per unit area in the separator $Q_{e,s}$ is not a function of the applied current, we retain the quadratic approximation ODE for its time-evolution.

In system identification, the input signal needs to be persistently exciting i.e., of sufficient amplitude and capable of exciting all salient modes. We chose a peak amplitude of 2C i.e., 120 A and applied the following input sequence to the P2D model

- 1) a Random Binary Signal (RBS) (0–199 s)
- 2) a swept cosine signal from 0–100 mHz (200–799 s)
- 3) a periodic Random Binary Signal with a period of 200 s and 2 such repeated periods (800–1199 s).

The ‘chirp’ (swept cosine) signal was designed to excite the low frequency (DC) modes of the electrolyte subsystem. The two RBSs target the poles and zeros that would typically be excited by highly dynamic input profiles. The periodicity in one of the RBSs was introduced to draw out any repeated real pole or complex conjugate poles. We included both low and high frequency spectra in the overall sequence to obtain a high degree of confidence in capturing the salient dynamics of the electrolyte subsystems. The training current profile is plotted in Fig. 4a.

Akin to any curve fitting (numerical regression) procedure, system identification is prone to overfitting the training data. In general, the ‘best’ transfer function that identifies a system is the lowest order model that not only minimizes the error on the training sequence, but also that on an independent validation sequence. Without this validation, the training error can be made arbitrarily small by using an unbounded number of poles and zeros in the transfer functions. However, such a model shall not generalize well to datasets outside the training realm since the true dynamics shall not have been identified. Our validation profile, visualized in Fig. 4b, consisted of the following sequence

- 1) a periodic Random Gaussian Signal (RGS) with 4 periods of 200 s each (0–799 s)
- 2) a Pseudorandom Binary Signal (PRBS) for emulating white noise i.e., with a flat power spectra across the frequency spectrum (800–999 s)
- 3) a multi-sine signal i.e., summation of sinusoids at various fundamental frequencies (1000–1199 s).

The mean of the training profile is $\bar{I}_{\text{train}} = -1.167$ A and that of the validation profile is $\bar{I}_{\text{val}} = -0.3273$ A. As a standard refinement, we used the de-biased signals, $\tilde{I}(t) = I(t) - \bar{I}(t)$ as the training and validation sequences. The corresponding de-biased output variables were $\tilde{Q}_{e,j}(t)$ obtained by subtracting their respective initial values $Q_{e,j}(0)$ from $Q_{e,j}(t)$

$$\tilde{Q}_{e,n}(t) = Q_{e,n}(t) - Q_{e,n}(0) \quad (24)$$

$$\tilde{Q}_{e,p}(t) = Q_{e,p}(t) - Q_{e,p}(0) \quad (25)$$

Therefore, $\frac{\tilde{Q}_{e,n}(s)}{\tilde{I}(s)}$ and $\frac{\tilde{Q}_{e,p}(s)}{\tilde{I}(s)}$ are to be identified.

C. Assumption 1 — isothermal behavior

As a simplifying assumption, all thermal dynamics of the cell have been neglected i.e., we seek to obtain an isothermal electrolyte concentration model at room temperature (298.15 K). In table I, (6) and (7) show the thermal dependence of the electrolyte's conductivity and diffusivity respectively. However, in line with the isothermal assumption, they have been deemed to have a spatio-temporal dependence only on the electrolyte concentration for the P2D model, while being held constant in all the ROM simulations in this work. Whilst acknowledging the limitation that this shall not capture the cell's dynamics at higher C-rates, we show in section IV that our proposed approach yields a model that has a much higher fidelity than the incumbent state-of-the-art in single particle modeling. In future works, we intend to relax this restriction and extend our approach to obtain a thermally coupled EECSPM.

D. Assumption 2 — linearity of subsystems

To aid the numerics of system identification, we assume that the subsystems to be identified are linear within the operating range. While at the macroscopic/system level, a Li-ion battery does exhibit overall non-linear characteristics owing to *a*) the Butler-Volmer kinetics, and *b*) the electrode Open Circuit Potentials (OCPs) (8) and (9). However, since we are dealing with a much narrower scope i.e., only the transfer functions mapping the input current. Therefore, it suffices to justify the linearity assumption for these two subsystems¹.

A linear system is one which obeys the superposition principle. For the task at hand, the following methodology was adopted

- 1) Apply an input profile $I_1(t)$ to the two subsystems and obtain outputs $\tilde{Q}_{e,n_1}(t)$ and $\tilde{Q}_{e,p_1}(t)$.
- 2) Apply a different input profile $I_2(t)$ to the two subsystems and obtain outputs $\tilde{Q}_{e,n_2}(t)$ and $\tilde{Q}_{e,p_2}(t)$.
- 3) Finally, apply a third input profile as a linear combination of the first two i.e., $I_3(t) = \alpha I_1(t) + \beta I_2(t)$ and obtain a corresponding set of outputs $\tilde{Q}_{e,n_3}(t)$ and $\tilde{Q}_{e,p_3}(t)$.
- 4) If the following relationship holds

$$\begin{aligned}\tilde{Q}_{e,n_3}(t) &= \alpha \tilde{Q}_{e,n_1}(t) + \beta \tilde{Q}_{e,n_2}(t) \\ \tilde{Q}_{e,p_3}(t) &= \alpha \tilde{Q}_{e,p_1}(t) + \beta \tilde{Q}_{e,p_2}(t)\end{aligned}$$

for all possible $\{\alpha, \beta\}$ and for all choice of input signals $\{I_1(t), I_2(t)\}$, then the subsystems are linear.

We performed 10 test simulations on the P2D model, employing random values for $\{\alpha, \beta\} \in [-1.25, 1.25]$ for each run. This limits the peak applied current to within a $\pm 3C$ window which helps to retain the validity of the isothermal assumption. Secondly, this keeps that the cell's SOC physically valid i.e., in (0%, 100%) even with the composite current during the test duration for a wide range of starting SOC's. Finally, the chosen window of C-rates helps to avoid localized saturation/depletion of ions. The signal $I_3(t)$ was obtained by taking a random linear combination of any two of the following step inputs for $I_1(t)$ and $I_2(t)$ — *a*) 1C discharge, *b*) discharge at %, *c*) 1C charge, and *d*) charge at %.

¹Signal debiasing is not relevant here since the mean values are constants.

Fig. 5. Illustration of one instance of linearity tests conducted for the subsystems under consideration. The top row of plot shows $\tilde{Q}_{e,n}$ and $\tilde{Q}_{e,p}$ for step inputs $I_1(t) = 60$ A and $I_2(t) = 12$ A i.e., discharge with 1C and C/5 currents respectively. The second row shows $\tilde{Q}_{e,n_3}$ and $\tilde{Q}_{e,p_3}$ for $I_3 = 36$ A, where $I_3 = \alpha I_1 + \beta I_2$ with $(\alpha, \beta) = (1, -2)$. The bottom row of plots overlays them with the linear combination of the two preceding responses. The transient responses in both regions closely track the superposition trajectory. Even past the transient, maximum error in both cases is an order of magnitude lower than the individual outputs. The two systems are deemed to be *approximately* linear.

Fig. 5 illustrates one instance of our linearity tests wherein plots in the left column depict the electrolyte time-evolution subsystem in the negative electrode region, while those in the right show its positive electrode region counterpart. The subsystem outputs with $I_1(t) = 60$ A i.e., 1C and $I_2(t) = 12$ A i.e., C/5 are plotted in the top row. With $(\alpha, \beta) = (1, -2)$, the composite input $I_3 = \alpha I_1 + \beta I_2 = 12$ A. The third row of plots show $\tilde{Q}_{e,n_3}$ and $\tilde{Q}_{e,p_3}$ overlaid with their linear combination counterparts $\alpha \tilde{Q}_{e,n_1} + \beta \tilde{Q}_{e,n_2}$. In the negative electrode region, the transient performance matches well until ≈ 450 s, whereas that for the positive electrode region exhibits good tracking for ≈ 250 s. The maximum absolute error in each region is $\mathcal{O}(10^{-4})$ even past the initial transient, an order of magnitude smaller than its individual components. This behavior was consistent for all test instances considered. Considering that for dynamic simulation runs, the transient performance is paramount to the performance of the model, these subsystems can be considered to be *approximately* linear for the operating conditions of interest.

A pristine cell can be considered as time-invariant owing to the absence of dominant degradation phenomena under standard operating conditions for at least the first few hundred cycles. Based on our analysis, a Linear Time-Invariant (LTI) behavior (for which a rich set of theory exists) for the two subsystems is therefore assumed, facilitating the numerics of the system identification procedure presented in section III-E.

E. Transfer function identification procedure

We have a classical discrete-time LTI identification problem

$$y[k] = G(z)u[k]; G(z) = z^{-n_k} \frac{b_1 z^{-1} + \dots + b_{n_b} z^{-n_b}}{1 + a_1 z^{-1} + \dots + a_{n_a} z^{-n_a}} \quad (26)$$

TABLE III

COEFFICIENTS OF FOUR DISCRETE-TIME TRANSFER FUNCTIONS IDENTIFIED FOR THE ELECTROLYTE TIME-EVOLUTION SUBSYSTEM IN THE NEGATIVE ELECTRODE REGION. THE FOURTH ORDER MODEL FROM CASE C (SHADED IN GRAY) PERFORMED THE BEST ACROSS BOTH TRAINING AND VALIDATION PROFILES.

Case	Numerator				Denominator				Training accuracy (%)	Validation accuracy (%)
	b_1	b_2	b_3	b_4	a_1	a_2	a_3	a_4		
A	0.0026	-0.0025			-1.922	0.923			95.11	95.13
B	0.0028	-0.0052	0.0025		-2.833	2.669	-0.836		99.14	98.54
C	0.0028	-0.0075	0.0066	-0.0019	-3.577	4.767	-2.801	0.612	99.73	99.28
D	0.0026	0.0026	-0.0024	-0.0024	0.060	-1.906	-0.058	0.907	95.12	95.14

The transfer function $G(z)$ is described by—1) number of transport delay samples n_k , 2) number of feedforward coefficients (zeros) n_b , 3) zeros themselves $b_1, b_2, \dots, b_{n_b}$, 4) number of feedback coefficients (poles) n_a , 5) pole locations $a_1, a_2, \dots, a_{n_a}$ to be determined for each of the two electrolyte time-evolution subsystems in the negative and positive electrode regions.

The system identification error can be defined as

$$\varepsilon[k] = y[k] - \hat{y}_m[k] \quad (27)$$

where $y[k]$ are true measurements

$$\hat{y}_m[k] = G(z)u[k] \quad (28)$$

and $\hat{y}_m[k]$ are outputs from the difference equation obtained using the transfer function models. The unknowns in $G(z)$ are collected into a parameter vector θ . Thus, as per (27), the notation of the error sequence parameterized by θ is amended to $\varepsilon[k; \theta]$. For an input-output data set with N samples, a generic cost function applicable to any parametric four model structure is

$$V_N(\theta) = \sum_{k=1}^N L(\varepsilon[k; \theta]) \quad (29)$$

where $L(\cdot)$ is a positive-valued scalar loss function.

The sum of squares of the error sequence may be used as a typical loss function, thereby yielding

$$V_N(\theta) = \sum_{k=1}^N \varepsilon^2[k; \theta] \quad (30)$$

The vector $\hat{\theta}$ that minimizes this cost function is desired i.e.,

$$\hat{\theta} = \arg \min_{\theta} V_N(\theta) \quad (31)$$

As a rudimentary estimation step for coefficient orders, we used an Auto Regressive with Exogenous Inputs (ARX) structure since (30) reduces to a standard quadratic optimization problem. For robustness against estimation bias, the Instrumental Variable (IV) method was employed, which yields two deterministic model order criteria— *a*) Akaike's Information Criterion (AIC), and *b*) Rissanen's Minimum Description Length (MDL) [40]. For the two subsystems under consideration, both criteria converged to the same values for the coefficient orders, yielding $n_a = 4$, $n_b = 4$ and $n_k = 0$. In the step responses of Fig. 5, we see that all outputs start exactly at zero, confirming $n_k = 0$ for both subsystems. These coefficient values reinforce our hypothesis that the first order time-evolution ODEs of (20) and (22) are indeed inadequate. These were hence used as the initial guesses for the coefficient orders in non-linear optimization algorithms used for determining the exact pole and zero locations.

The ARX model structure is too simplistic and typically produces poor estimates of the system's poles and zeros. Since we have noise-free simulation outputs (from the P2D model), the Box-Jenkins and Output Error (OE) structures were deemed unnecessary. Therefore, we consider only the Auto Regressive with Moving Average and Exogenous Inputs (ARMAX) model structure, wherein the non-linear cost function of (30) was minimized iteratively using quasi-Newton methods. A randomized multi-start algorithm was used to seed the initial guesses of the coefficients $\{a_1, a_2, \dots, a_{n_a}\}$ and $\{b_1, b_2, \dots, b_{n_b}\}$. Since the magnitudes of $\tilde{Q}_{e,n}$ and $\tilde{Q}_{e,p}$ are of $\mathcal{O}(10^{-3})$, a constant factor of $k = 1000$ was used to scale the order of magnitude of output data values to unity. The system identification procedure was performed on a 64-bit Hewlett-Packard Z840 workstation with a 16-core Intel® Xeon® E5-2640 v3 (Haswell) processor clocked at 2.60 GHz with 128 GB DDR4 RAM at 1866 MT/sec. The software used for the identification process was MATLAB R2018a System Identification Toolbox [41]. However, a single core with a working memory of ≈ 970 MB was sufficient to run the identification process to completion.

Table III shows the coefficients obtained by the identification routine for the time-evolution subsystem in the negative electrode region. We retained only those models that yielded similar errors (within 0.5 %) across both input datasets. Since first order transfer functions were deemed to be inadequate, the lowest order tried in the identification procedure was two (case A). We seek the lowest order model that produces the highest matched accuracy across both training and validation profiles. Case D illustrates the importance of the initial values used in non-linear optimization algorithms. Despite using the same number of coefficients as case C, we converge to a radically different set of zeros and poles resulting in a percentage error comparable to that of the simple second order case A. The fourth order model from case C (shaded gray) performs the best across both training and validation profiles and is chosen as the final model. We applied a similar selection procedure for the transfer function identification of the $\tilde{Q}_{e,p}$ subsystem in the positive electrode region. Its coefficients obtained were $b_1 = -0.0028$, $b_2 = 0.0071$, $b_3 = -0.0059$, $b_4 = 0.0016$; $a_1 = -3.464$, $a_2 = 4.444$, $a_3 = -2.495$, $a_4 = 0.515$.

The poles of $\tilde{Q}_{e,n}$ are at (0.9969, 0.9870, 0.9106, 0.6829) while those of $\tilde{Q}_{e,p}$ lie at (0.9967, 0.9880, 0.8952, 0.5842) on the Z-plane i.e., close to each other and hence exhibiting comparable dynamics. The slight differences in the pole locations could be attributed to variations in the physical parameters pertaining to the two electrode regions. The zeros of the two subsystems are close to each other while their signs are opposite. This is in

congruence with the step response plots in Fig. 5, where $\tilde{Q}_{e,n}$ and $\tilde{Q}_{e,p}$ evolve in opposite directions. The opposing signs in zeros agree with the fact that a decrease in ions in the negative electrode region must be accompanied by an increase in its positive electrode counterpart and vice-versa (however, the changes shall not be equal owing to the presence of the separator region). The identified transfer functions are thus consistent and deemed to be suitable for representing the electrolyte time-evolution.

IV. RESULTS AND DISCUSSION — SYSTEM IDENTIFICATION MODEL FOR ELECTROLYTE CONCENTRATION DYNAMICS

In this section, we discuss the results of using the system identification model of electrolyte concentration for constant current and dynamic load profiles. We compare the performance of our proposed model to that of the quadratic approximation model, whilst using the P2D model as the reference benchmark.

A. Constant current input

Fig. 6 shows the spatial distribution of ionic concentration along the cell's thickness for a 1C discharge starting at 100 % SOC, computed by the P2D, quadratic approximation and system identification models. The P2D model exhibits a characteristic inflection near the separator interfaces initially that diffuses out over time. This is because the reaction fronts are initially established close to the separator, and as surface concentration of lithium in particles near separator is depleted, it moves further back into the electrodes towards the current collectors. Neither of the two ROMs under consideration here could capture this phenomenon. This is explained by the fact that both ROMs use a quadratic profile for their *spatial* profiles, meaning that only one apex point is mathematically possible per electrode,

Fig. 6. Spatial distribution of ionic concentration in electrolyte along cell thickness at various snapshots of time computed by each of the three models for a 1C discharge. The concentration profile computed by the P2D model is used as the benchmark reference. The system identification model performs noticeably better than the quadratic approximation model during the transient phase while both ROMs deliver a similar performance after the initial transient.

which is pinned to their separator interfaces as per the equations used. During the transient phase (lasting up to ≈ 357 s), the loci of concentration profiles of the system identification model lie closer to the P2D output than that computed by the quadratic model. Thereafter, both ROMs follow similar trajectories.

This behaviour of improved *transient response* and similar steady-state performance relative to the quadratic model is reflected in Fig. 7 which presents a temporal perspective of ionic concentration evolution at the two current collectors. The left column of Fig. 7 corresponds to the negative current collector interface while the right column corresponds to its positive counterpart. The bottom row shows the time-evolution of the absolute value of the errors of the two ROMs with respect to the benchmark P2D output. The error of the system identification model remains strictly below that of the quadratic model until ≈ 650 s at the negative electrode/current collector interface, and for ≈ 3300 s at its positive counterpart. Once the reaction front diffuses out and a steady rate of ion-electron separation/recombination is established, the spatial description dominates. This explains the similar shapes of the two ROMs past the initial transient. These results imply that the models identified here are especially suitable for transient i.e., dynamic load profiles, typically seen in xEV applications.

B. Dynamic current inputs

To characterize the temporal performance under dynamic load conditions, the UDDS drivecycle with a peak amplitude of 180 A i.e., 3C was used. The top row of Fig. 8 shows the time evolution of ionic concentration computed by the three models under consideration at the two current collectors. The left column pertains to the negative current collector while the right column corresponds to its positive counterpart. The bottom row shows the absolute value of concentration errors of the two ROMs relative to the P2D reference benchmark, wherein the error of the system identification model remains below that of the quadratic model throughout the drivecycle.

Fig. 7. Time evolution of ionic concentration at the two current collectors with a 1C discharge current for a) the P2D model, b) the quadratic approximation model, and c) the newly developed system identification models (top row). For the quadratic approximation and system identification models, the time evolution of their absolute error relative to the P2D benchmark is also shown (bottom row). At both current collectors, the transient performance (also shown in the insets) of the system identification model is superior to the quadratic approximation model. Thereafter, both ROMs deliver a relatively similar performance.

Fig. 8. Evolution of ionic concentration over time at the two current collector interfaces with a UDDS input profile as computed by the *a*) P2D, *b*) quadratic approximation, and *c*) system identification models (top row). The plots on the left pertain to the negative electrode/current collector interface, while that on the right corresponds to its positive counterpart. For the quadratic approximation and system identification models, their absolute error relative to the P2D benchmark is also shown (bottom row). The system identification model is considerably more accurate than the quadratic model for the entire time horizon of the drivecycle.

TABLE IV

ERROR STATISTICS COMPARING THE TEMPORAL PERFORMANCE OF THE QUADRATIC AND SYSTEM IDENTIFICATION MODELS. THE ERROR METRIC IS THE ABSOLUTE VALUE OF THE CONCENTRATION DIFFERENCE OF THE ROMs AND THE P2D MODEL AT THE TWO CURRENT COLLECTORS.

Input Profile	Error statistic (mol/m ³)	ε _{cc} at Neg/CC		ε _{cc} at Pos/CC	
		Quadratic	SysID	Quadratic	SysID
1C discharge	Max	133.80	39.51	276.33	194.27
	Mean	48.16	29.56	227.92	146.53
	Median	25.60	30.17	218.96	173.14
	Std. Deviation	36.94	8.22	29.71	55.79
UDDS	Max	307.27	190.04	292.20	114.44
	Mean	66.38	54.98	55.15	25.02
	Median	49.65	47.12	40.39	20.93
	Std. Deviation	66.80	37.18	60.50	20.17

In particular, when a current spike is applied at ≈ 200 s, the quadratic model is unable to cope and its absolute error deviates far away from its mean value. However, the system identification model's error trajectory remains well controlled and even with such instantaneous load demands, its standard deviation is close to its median value. Table IV provides a summary of error statistics for the 1C constant current and UDDS input profiles.

V. AN ELECTROLYTE-ENHANCED COMPOSITE SINGLE PARTICLE MODEL (EECSPM) OF A LI-ION CELL

Once its spatio-temporal concentration is available, we may use (5) to compute the electrolyte overpotential. In this work, we use the *initial* concentration to compute ionic conductivities in the ohmic contribution to electrolyte overpotential throughout the entire time horizon. Hence, (5) gets modified as

$$\phi_{e_p}(t) - \phi_{e_n}(t) = (1 - t_+^0) \frac{2RT}{F} \ln \frac{c_{e_p/cc}(t)}{c_{e_n/cc}(t)} - \frac{I}{2A} \left(\frac{l_n}{\kappa_{eff_n}(c_{e,0})} + \frac{2l_s}{\kappa_{eff_s}(c_{e,0})} + \frac{l_p}{\kappa_{eff_p}(c_{e,0})} \right) \quad (32)$$

thereby implying that the system identification model influences only the first term of (32).

Fig. 9 quantifies the relative contributions to the electrolyte overpotential from each of the two terms in (32) for a 1C discharge. The bulk solution resistance is constant since the initial electrolyte concentration is used in computing the effective ionic conductivities in the three regions of the cell. However, it is the gradient-induced diffusion polarization that has the major contribution during the entire time horizon, and entirely governing the transient phase response. Hence, we deem it appropriate to simplify the model computations by simply using the initial concentration for the ohmic contribution.

Fig. 10 shows the electrolyte overpotential profiles for a UDDS input sequence. The system identification model exhibits a good tracking of the P2D model's trajectory with a Mean Absolute Error (MAE) of 15.88 mV (8.19 %) and a Root Mean Square (RMS) error of 24.11 mV (12.44 %).

Fig. 9. Relative contributions to the electrolyte overpotential from the bulk and polarization resistance for a 1C discharge. The bulk solution resistance is approximated as a constant value corresponding to the conductivity at the equilibrium initial concentration. The concentration-dependent polarization entirely governs the transient behavior of the overall overpotential, while having a strong contribution at the steady state, much higher than the bulk resistance.

Fig. 10. Comparison of electrolyte overpotential computed by the P2D model and the system identification model for a UDDS load profile. The overpotential profile computed by the system identification model has a fairly good match with that obtained by the P2D model and has a Mean Absolute Error (MAE) of 15.88 mV and a Root Mean Square (RMS) error of 24.11 mV.

The electrode overpotentials are given by

$$\eta_p = \phi_{s,p} - \phi_{e,p} - U_p \quad (33)$$

$$\eta_n = \phi_{s,n} - \phi_{e,n} - U_n \quad (34)$$

wherein contributions of the electrolyte potential terms are now included. Subtracting (34) from (33) and rearranging,

$$V_{\text{cell}} = \eta_p - \eta_n + \underbrace{\phi_{e,p} - \phi_{e,n}}_{\Delta\phi_e} + U_p - U_n. \quad (35)$$

By embedding the electrolyte overpotential difference into the voltage calculation and retaining all other equations of the basic SPM framework (1)–(3f), we obtain the EECSPM, whose performance is quantified in section VI.

VI. RESULTS AND DISCUSSION

In this section, we present plots comparing the voltage accuracies (for constant current and dynamic inputs) of — *a*) the EECSPM, and *b*) the basic SPM, with the P2D model serving as the reference benchmark. In order to quantify the gains of the EECSPM over the incumbent state-of-the-art, the performance of the quadratic approximation SPM is also tabulated.

A. Constant current inputs

The left plot of Fig. 11 shows the terminal voltage outputs of various SPMs for a 1C discharge beginning at 100 % SOC. Since it does not account for electrolyte overpotentials, the output voltage of the basic SPM lies above that of the benchmark P2D model. On the contrary, the EECSPM over compensates for the electrolyte overpotential and its terminal voltage lies below the P2D output. Hence, in order to compare their performance, it is appropriate to use the absolute value of their errors with respect to the P2D benchmark. The plot in the right of Fig. 11 shows the percentage deviation of the absolute error of the two ROMs.

B. Dynamic inputs

Fig. 12 shows the output voltage of all models under consideration for a UDDS input profile with an amplitude of 180 A (3C). A zoomed view of the voltage responses during a small time-window is also shown, highlighting that the EECSPM tracks the complex shape characteristics (kinks, crests and troughs) of the P2D model while staying close to its magnitude.

Fig. 11. Voltage output of various SPMs for a 1C discharge. The basic SPM's output lies above that of the benchmark P2D model owing to lack of electrolyte overpotential, while the EECSPM over compensates for it so that its terminal voltage lies below the P2D output. The EECSPM performs significantly better with a peak absolute error of $\approx 4\%$ in contrast to almost 11% for the basic SPM.

Fig. 12. Voltage output of the composite EECSPM for a UDDS input profile with a peak magnitude of 180 A (3C). The voltage profiles computed by the basic SPM and the benchmark P2D model is also overlaid. It is seen that the composite EECSPM is significantly more accurate than the basic SPM.

TABLE V
SUMMARY OF STATISTICS FOR THE PERCENTAGE ABSOLUTE ERROR IN TERMINAL VOLTAGE FOR THE BASIC SPM, QUADRATIC SPM AND THE EECSPM FOR CONSTANT CURRENT AND DYNAMIC INPUTS.

Input Profile	Error Statistic for $ \varepsilon_v $	Basic SPM	Quadratic SPM	SysID EECSPM
1C discharge	Worst case	10.67	5.83	4.05
	Mean	2.92	1.79	1.54
	RMS	3.27	2.31	1.65
UDDS	Worst case	2.59	1.68	0.72
	Mean	0.51	0.36	0.11
	RMS	0.68	0.39	0.16

Table V shows a summary of the percentage absolute error statistics, additionally including the performance metrics from the quadratic approximation SPM for both constant current and dynamic inputs. In both cases, for every error statistic considered, the EECSPM performs better than the two other ROMs. In particular, the percentage improvement in terminal voltage accuracy is at least twice of that of the state of the art quadratic SPM, and represents a significant improvement to the modelling art.

Finally, we discuss the wider applicability of our proposed procedure to a general physical cell. Our approach was based on applying the system identification methodology to the niche, yet carefully constructed temporal subsystems of the electrolyte concentration dynamics, which is hard to validate experimentally. While our chosen input current sequences can be synthesised using standard lab equipment as a programmable battery cycler, the output measurements (moles of Li^+ per unit cross-sectional area) are to be computed by integrating over the electrode thicknesses the electrolyte spatial concentration profiles which are non-trivial to measure experimentally. Hence, this approach may be ported to a real physical cell (through an identical simulation-based study) only if its relevant physical parameters, as required by the P2D model, are available.

VII. CONCLUSIONS

While the use of the system identification-based EECSPM for prolonged high C-rate operations needs further exploration, it is

indeed deemed to suitable for dynamic load profiles, even those with large magnitudes of instantaneous charge or discharge. Prima facie, while the accuracy improvements to the spatio-temporal electrolyte concentration profile *per se* appears to be relatively small, the keen observation here is that this facilitates an improved computation of electrolyte overpotential, which in-turn leads to an improved accuracy in a key quantity *viz.* the model's terminal voltage. In SOC estimators, owing to flatness of the voltage-SoC relationship in typical automotive-grade cell chemistries, even a small perturbation in the computed model voltage shall map to a radically different SoC operating point [4]. Therefore, taking cognizance of this highly sensitive influence of voltage on the cell's SoC, the improvements to the plant model proposed in this work shall significantly aid in improved state estimator designs.

Thus, we conclude that the EECSPM developed here does indeed represent an advancement to the SPM modeling art, and may be employed as the plant model in state estimation and control applications in a vehicular BMS. Although the treatment here pertains to an isothermal implementation, we acknowledge the crucial influence of thermal dynamics on the cell's behavior. Future work shall explore the application of system identification techniques to thermally coupled models.

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